UNITED STATES DEPARTMENT OF COMMERCE
HARRY L. HOPKINS, Secretary
NATIONAL BUREAU OF STANDARDS
Lyman J. Briggs, Director

✦

Journal of Research

of the

National Bureau of Standards

✦

Volume 25, Number 4

October 1940

[Published with approval of the Director of the Budget]

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1940

For sale by the Superintendent of Documents, Washington, D. C. - - - - - - Price 30 cents
$3.50 per year on subscription

The prices of the separate Research Papers appearing in this JOURNAL are given on the front cover page. If 100 or more copies of any separate are ordered, a discount of 25 percent is allowed. Those who desire copies of separate Research Papers should send their orders and remittances without delay to the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. This will aid him to determine the number of copies to be printed for sale. Research Papers are not printed from electrotypes, and usually no more reprints can be had when the first and only printing is exhausted.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1333

Part of Journal of Research of the National Bureau of Standards, Volume 25, October 1940

DETERMINATION OF NONVOLATILE MATTER AND THE CALCULATION OF "CUT" OF SHELLAC VARNISH

By Charles C. Hartman

ABSTRACT

Using the three recognized methods for determining the nonvolatile content of shellac varnish, 70 varnishes, made by cutting 33 dry orange shellacs and 6 dry bleached shellacs in 5 different solvents, were examined and a summary of the results was prepared. This summary shows: (1) That the method given in Federal Specification TT–V–91 is most convenient and simple in operation, and that the results obtained thereby are in closer agreement than those obtained by the methods given in the specifications of the American Society for Testing Materials and of the U. S. Shellac Importers Association, Inc.; (2) That the presence of volatile matter in dry shellac and the use of solvents with high end points influence, decidedly, the nonvolatile determination; and (3) That, in calculating the "cut" of a shellac varnish, a positive correction must be made to the percentage of nonvolatile residue for the volatile content of the dry shellac determined at 105° C.

CONTENTS

	Page
I. Introduction	395
II. Materials used	396
1. Shellac	396
2. Volatile components	398
III. Preparation of experimental varnishes	398
IV. Determination of nonvolatile content	398
V. Discussion of results and conclusions	401
VI. References	402

I. INTRODUCTION

By the term "shellac varnish" is understood the material defined by the American Society for Testing Materials [1] [1] as "A solution or 'cut' of a specified grade of pure orange shellac or dry bleached shellac (the manufactured products from the secretion of the *Laccifer Lacca Kerr* with no added resin, copal or other adulterants) in the most commonly used solvent, 95 percent (190 proof) specially denatured alcohol, Formula 1 of the U. S. Internal Revenue Bureau or in other specified denatured alcohol or solvent." The refinement of the natural resin to produce the orange shellac used in varnish making is largely a cleaning process to remove excessive dirt and sticks [2]. Bleached shellac is obtained by treating orange shellac with chemical agents to remove the natural dye. Various grades of orange and bleached shellac varnish are available in "cuts" ranging from 3 to 8 pounds. In the trade, the word "cut" indicates the pounds of shellac resin added to each gallon of solvent. The manufacturer's label on the

[1] Figures in brackets indicate the literature references at the end of this paper.

container usually states the cut of the shellac varnish; for example, "4 pounds per gallon" or "4-pound cut." This statement does not mean that the gallon of varnish contains 4 pounds of shellac resin but indicates that 4 pounds of "dry" [2] shellac was dissolved, or cut, in 1 gallon of solvent. About 1.4 gallons of varnish results, and hence 1 gallon of this varnish contains slightly less than 3 pounds of the dry shellac—equivalent approximately to 37 percent by weight.

The amount of shellac in the varnish is determined by evaporating the solvent under specified conditions and assuming that what is left is shellac. Three procedures are now in use for this purpose: those of the United States Shellac Importers Association (abbreviated USSIA) [1], of the American Society for Testing Materials (ASTM) [3], and of the United States Government (FS for Federal specification) [4]. In each procedure a 1.0- to 1.5-g sample of varnish is weighed into a shallow metal dish and is heated in an oven at a constant temperature of about 105° C for a specified period of time and again weighed. Differences in the methods are shown in table 1. It was the purpose of the tests reported in this paper to ascertain how well the amounts of shellac found in varnishes by each of the three methods agree with the amounts measured when the varnishes are manufactured. Briefly, the method of study consisted in dissolving weighed quantities of numerous grades of shellac in different solvents, and determining the nonvolatile matter in the resultant varnishes by the three methods in question.

TABLE 1.—*Differences in methods*

Method	U. S. Shellac Importers Association, Inc.	American Society for Testing Materials	Federal specification
Receptacle	Tin-foil dish approximately 1¼ in. (3.1 cm) in height and 2½ in. (6.3 cm) in diameter.	Friction-top can plug approximately 5/16 in. (0.8 cm) in height and 3.2 in. (8 cm) in diameter.	Friction-top can plug approximately 5/16 in. (0.8 cm) in height and 3.2 in. (8 cm) in diameter.
Weight of sample	About 1 g	Not more than 1.5 g	1 to 1.5 g.
Addition of sand	10 g	10 g	None.
Addition of specially denatured alcohol (formula 1).	1 ml to "cuts" heavier than 5 pounds.	Approximately 2 g	Do.
Treatment before heating.	Sand and varnish mixed thoroughly with glass rod.	Sand and varnish mixed thoroughly with glass rod.	Do.
Temperature at which heated.	105° ±2° C	105° ± 2°C	105° to 110° C.[a]
Heating period	1 hour	3 hours	3 hours.

[a] The revision of this specification now in the process of being printed specifies a temperature of 105° ±2° C.

II. MATERIALS USED

1. SHELLAC

Thirty-three samples of orange shellac of thirty different commercial brands or grades, four samples of "regular" and two samples of "refined" bleached shellac were used. Since determinations were to be made of the nonvolatile residue, a knowledge of the amount of volatile matter in the original shellac was essential to an interpretation of the results. The method most commonly used for determining volatile matter—usually considered to be moisture—is to heat a finely ground sample in a shallow dish to constant weight at a

[2] With ordinary shellac, the term "dry" refers to the shellac as sold.

TABLE 2.—*Volatile content of "dry" shellacs*

Identification number	Loss of weight at—	
	41°±2° C (24 hr)	105°±2° C (3 hr)
1. ORANGE SHELLAC		
	Percent	*Percent*
1 (a) [1]	0.38	1.32
1 (b)	.41	1.31
1 (c)	.54	1.42
2 (a)	.26	1.17
2 (b)	.52	1.31
3	.45	1.50
4	.48	1.52
5	.36	1.36
6	.56	1.38
7	.68	1.45
8	.58	1.40
9	.49	1.37
10	.34	1.30
11	.37	1.35
12	.38	1.34
13	.38	1.42
14	.31	1.43
15	.34	1.44
16	.44	1.36
17	.44	1.41
18	.59	1.52
19	.52	1.48
20	.60	1.56
21	.29	1.58
22	.45	1.58
23	.82	1.34
24	.86	1.44
25	.82	1.37
26	.79	1.27
27	.70	1.39
28	.81	1.44
29	.70	1.40
30	.76	1.42
Average	0.53	1.41
Avg deviation	.15	.07
Max minus min	.60	.41
2. BLEACHED SHELLAC (REGULAR)		
31	0.75	1.93
32	4.77	5.69
33	2.04	3.03
34	4.28	4.97
3. BLEACHED SHELLAC (REFINED)		
35	2.48	3.31
36	5.54	6.12
Average, 2 and 3	3.31	4.18
Avg deviation, 2 and 3	1.54	1.25
Max minus min, 2 and 3	4.79	4.19

[1] Letters in parentheses indicate samples of the same grade of shellac.

temperature of 41° ±2° C. However, it is known that the loss increases with the temperature of drying, and since the determination of the nonvolatile content of the varnish is made at 105° C, the loss at this temperature seemed more informative. Consequently, samples

of 0.25 to 1.00 g of the finely ground shellac in friction-top can plugs were heated at 105° C for 3 hours. In table 2 these results are compared with those found by heating at 41° C for 24 hours.[3]

2. VOLATILE COMPONENTS

The solvents used in cutting the dry shellacs were those authorized for this purpose by the United States Bureau of Internal Revenue [5] as follows:

(1) Formula 1.—100 gallons of ethyl alcohol (190 proof) denatured with 5 gallons of approved wood alcohol.

(2) Formula 1A.[4]—100 gallons of ethyl alcohol (190 proof) denatured with 10 gallons of denaturing grade isopropanol and 0.5 gallon of commercial alpha-terpinol.

(3) Formula 44A (1).[4]—100 gallons of ethyl alcohol (190 proof) denatured with 4 gallons of approved wood alcohol and 10 gallons of normal butyl alcohol.

(4) Formula 44A (2).[4]—100 gallons of ethyl alcohol (190 proof) denatured with 4 gallons of approved wood alcohol and 10 gallons of amyl alcohol (synthetic or natural).

(5) Proprietary solvent.—Made to standard Alcohol Tax Unit formula: 100 gallons of specially denatured alcohol formula 1, 5 gallons of denatured ethyl acetate, and 1 gallon of aviation gasoline.

III. PREPARATION OF EXPERIMENTAL VARNISHES

The orange shellacs were ground to pass a 40-mesh sieve, and the bleached shellacs were powdered. A portion of each shellac after thorough mixing, was weighed accurately in a tared glass container, the solvent was added, and the container was stoppered tightly and reweighed. The varnishes were stored at room temperature for several days and, to insure complete solution, were shaken periodically. The following is a list of the solutions made:

(1) 30 orange and 6 bleached shellacs in alcohol denatured according to formula 1.

(2) 5 orange shellacs in alcohol denatured according to formula 1A.

(3) 5 orange shellacs in alcohol denatured according to formula 44A (1).

(4) 4 orange shellacs in alcohol denatured according to formula 44A (2).

(5) 6 orange and 6 bleached shellacs in the proprietary solvent.

(6) 4 orange shellacs (previously heated to 41°±2° C for 24 hours) in alcohol denatured according to formula 1.

(7) 4 orange shellacs (previously heated at 41° ±2° C for 24 hours) in the proprietary solvent.

IV. DETERMINATION OF NONVOLATILE CONTENT

Three determinations of the nonvolatile content of each varnish were made by each of the three methods mentioned in the introduction. The heating was done in an electric oven which had four revolving shelves. The three receptacles containing the samples of any

[3] 3 to 6 hours is the time usually employed for the test at 41° C.

[4] Since this work was undertaken a revision of the regulations has been issued. Formulas 1A and 44A (2) have been discontinued. Formula 44A (1) has been changed to formula 44 which reads: "To every 100 gallons of ethyl alcohol (190 proof) add 10 gallons of normal butyl alcohol."

one varnish to be tested by the three methods were placed on the same shelf, and the three tests were begun simultaneously. On different days the tests of the same varnish were repeated, with the three specimens placed on a different shelf each time.

The FS method gave the best agreement between triplicate tests. This is shown by the summary in table 3.

The weighed residues, and the same corrected in each case by adding the loss of weight at 105° C of the dry shellac used in making the varnish, were both expressed as percentages of the weights of shellac dissolved. A complete tabulation of the results, expressed on this percentage basis, is too long to be included in this paper, but table 4 summarizes them as the minimum, maximum, and average for each group of varnishes. The "corrected" percentage would have been 100 in each case if all the solvent had evaporated and the residue had been brought to the same state as that of the dry shellac after being heated at the same temperature.

TABLE 3.—*Agreement between results obtained in triplicate determinations of nonvolatile residues in 70 varnishes*

Method	Federal specification	American Society for Testing Materials	U. S. Shellac Importers Association, Inc.
Minimum difference between the highest and lowest results obtained in any triplicate set.....percent..	0.02	0.05	0.07
Maximum difference between the highest and lowest results obtained in any triplicate set.....percent..	.58	.77	1.12
Average of differences between the highest and lowest results obtained in all the triplicate sets.....percent..	.19	.25	0.34
Number of triplicate determinations in which the difference between the highest and lowest results exceeded 0.34%....	5	25	32

The USSIA method gave high values consistently, probably because of insufficient time of heating and consequent retention of solvent. The FS and ASTM methods also gave high values for the varnishes which contained solvent formulas 44A (1) and 44A (2). Both of these formulas contain appreciable amounts of solvents with high "end points," [5] and again, retention of solvent seems to explain the results.

[5] The term "end point" refers to the temperature at which the last portion of the solvent mixture evaporates in a distillation test. In this work, 110° C is chosen as a reasonable minimum temperature.

TABLE 4.—*Minimum, maximum, and average percentages of nonvolatile residues recovered from the shellac varnishes by three different methods*

Solvent formula (see p. 398 of text)	Type of shellac varnish	Number of varnishes represented	Average percentage of volatile matter found in the dry shellac at 105° C	Method	Percentage of recovery			Average percentage of recovery, corrected for percentage of volatile matter in the dry shellac at 105° C
					Minimum	Maximum	Average	
			%		%	%	%	%
1	Orange	30	1.4	FS	97.5	99.2	98.4	99.8
				ASTM	97.5	99.6	98.5	99.9
				USSIA	97.7	100.8	99.3	100.7
Proprietary	do	6	1.3	FS	97.7	99.5	98.8	100.1
				ASTM	97.9	99.2	98.7	100.0
				USSIA	98.6	99.7	99.3	100.6
1A	do	5	1.4	FS	98.2	99.2	98.8	100.2
				ASTM	98.2	99.1	98.6	100.0
				USSIA	98.7	100.2	99.3	100.7
44A (1)	do	5	1.4	FS	98.6	101.1	99.9	101.3
				ASTM	98.6	99.9	99.3	100.7
				USSIA	99.7	101.0	100.5	101.9
44A (2)	do	4	1.6	FS	98.9	99.6	99.3	100.9
				ASTM	98.4	99.2	98.9	100.5
				USSIA	100.0	100.7	100.3	101.9
1	Bleached	6	4.2	FS	93.7	98.7	95.7	99.9
				ASTM	93.8	98.3	95.7	99.9
				USSIA	95.3	99.5	96.8	101.0
Proprietary	do	6	4.2	FS	93.3	98.0	95.3	99.5
				ASTM	93.5	97.8	95.4	99.6
				USSIA	94.8	98.8	96.7	100.9

V. DISCUSSION OF RESULTS AND CONCLUSIONS

In table 2 the volatile portion of dry shellac is listed as determined at 41° C and at 105° C. The considerable variation in the results obtained at 41° C can be attributed not only to the variable moisture content of the original samples because of day to day differences in the relative humidities of the room in which they were stored but also to the fact that the relative humidity of the drying oven at a temperature of 41° C will vary over a wide range according to the relative humidity in the room at the time of the determination. The better agreement in the values obtained at 105° C for the orange shellacs can be attributed to the practical elimination of the relative humidity of the oven as a factor in the results obtained.

When corrected for the volatile material in the shellac, the ASTM and FS methods for nonvolatile material in the varnish agree well with each other and with the amount of dry shellac used, at least if nothing less volatile than ethyl alcohol is in the solvent. The weights of the residues from the shellac varnishes containing less volatile solvents are in approximately the same order as the end-point temperatures of the solvents used. That the use of the most volatile solvent (the proprietary one) resulted in the recovery of slightly less than the weight of dried bleached shellac used is not surprising in view of the fact that the addition and subsequent evaporation of a very volatile solvent has long been in use for the removal of less volatile material from very viscous and colloidal material in general. The fact that triplicate tests of the same varnishes by the FS method gave slightly more concordant results than by the ASTM method may make it preferable. Its greater convenience and simplicity are additional and probably more important reasons for using it.

Because the amount of volatile material in dry shellac varies, it is impossible to determine by analysis the exact weight of the dry shellac that was cut in a gallon of solvent. However, the analyst can obtain an approximate value for the cut by making a positive correction on the nonvolatile residue, using arbitrary values for the volatile content of the dry shellac. The arbitrary values found to be most satisfactory for this estimation are 1.4 percent for orange shellacs and 4.2 percent for bleached shellacs.

Specifications to be significant should state the percentage of nonvolatile material in a shellac varnish, dried at 105° C, as the Government specifications do, and not the cut of the varnish.

Appreciation is expressed to members of the Bureau's paint section for their helpful advice, and to Wm. H. Gardner, of the Shellac Research Bureau, Brooklyn, N. Y., for furnishing representative samples of bleached shellac.

VI. REFERENCES

[1] Official Methods of Analysis, Specifications, and General Information on Shellac and Bleached Shellac, Approved by the U. S. Shellac Importers Assoc., Inc., and the American Bleached Shellac Manufacturers Assoc., Inc., N. Y. The United States Shellac Importers Assn., Inc., New York, N. Y. (1934).
[2] C. C. Hartman, BS J. Research **7**, 1105 (1931) RP391.
[3] Book of Standards, 1939, part 2, Nonmetallic Materials, Constructional. American Society for Testing Materials, Philadelphia, Pa. (1939).
[4] Federal Specification for Varnish; Shellac. U. S. Government Printing Office, Washington, D. C. (May 26, 1931).
[5] Formulae for Completely and Specially Denatured Alcohol, Appendix No. 3 (1938). U. S. Bureau of Internal Revenue. U. S. Government Printing Office, Washington, D. C. (1939).

WASHINGTON, May 15, 1940.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1334

Part of Journal of Research of the National Bureau of Standards, Volume 25, October 1940

METHOD FOR DETERMINING THE MOISTURE CONDITION IN HARDENED CONCRETE

By G. Rupert Gause and John Tucker, Jr.

ABSTRACT

A method for studying the moisture conditions inside hardened concrete and cement paste is described. An electric hygrometer developed by the National Bureau of Standards was used to measure the relative humidity in cavities at various locations in the material. The relative humidity inside 12-inch concrete cubes stored at 50 percent relative humidity for 300 days was found to range from 50 percent near the surface to 66 percent near the center of the cube. For cubes stored at 20-percent relative humidity the corresponding range was from 20 to 60 percent. The relative humidity over cement paste of approximately normal consistency and cured in hermetically sealed bottles for 28 days was found to be 88 percent for a moderate heat-of-hardening cement and 79 percent for a high-early-strength cement.

CONTENTS

	Page
I. Introduction	403
II. Description of hygrometer	404
III. Scope of tests	405
IV. Tests	407
1. Relative humidity within concrete exposed to drying	407
2. Relative humidity inside hermetically sealed specimens	413
(*a*) Effect of temperature	413
(*b*) Effect of setting and hardening of cement paste	414
V. Accuracy of method	415
VI. Summary and conclusions	415
VII. References	416

I. INTRODUCTION

It has long been recognized that the moisture condition of concrete affects the volume changes, rate of hardening, and strength of concrete, as well as the life of coatings such as paint or linoleum, applied to the surface of the concrete. In laboratory tests changes in the moisture condition of concrete are usually obtained by weighing the specimen, any change in weight being assumed to be a loss or gain in water content. Since changes in the chemical or physical state of water in a concrete do not change the weight of the concrete, this method cannot measure changes in the moisture condition produced by hydration of the cement or by changes in the capillary structure of the concrete. On the other hand, carbonation at and near the surface of the concrete does change the weight without changing the water content, and this effect may be relatively large in the case of small specimens.

In the field, or where the moisture condition of concrete *in situ* is desired, the method lately developed by Spenser [1] [1] is the only one

[1] Figures in brackets indicate literature references at the end of this paper.

giving quantitative results. This method consists in measuring the electrical conductance of the concrete and comparing it with the conductance of a sample of the same concrete cured without loss or gain of water. The results are expressed in terms of "percent available moisture lost", the total available moisture being defined by Spencer as the weight lost upon prolonged storage at 25-percent relative humidity and 70°F. Spenser presents a calibration curve whereby the conductance measurements can be translated into "percent available moisture lost" units, thus eliminating the need for any weight measurements. This method, since it is a measure of weight changes, has the limitations of the laboratory weighing method and also several additional limitations which were pointed out by Spenser.

Davis [2] has shown that the shrinkage and expansion of concrete are closely related to the relative humidity of the air in which the concrete is stored. Jesser [3] has found that the vapor pressure of set cement decreases as the cement is dried and that the change is partly reversible. These relationships between the vapor pressure of set portland cement and both its water content and its volume changes are perhaps the strongest evidence upon which the colloidal theory of the setting and hardening of portland cement is based. Colloids lose water as the relative humidity of the surrounding air is decreased and reach a condition of equilibrium corresponding to each relative humidity. It is also well known that fine sands and soils may contain several percent of moisture while in equilibrium with air at a relative humidity of 90 percent, and the equilibrium relative humidity of soils has been suggested as a measure of their moisture content [4].

From the above it is apparent that the relative humidity inside concrete and cement pastes (i. e., in a cavity within the mass) may be of considerable importance. Since the relative humidity inside concrete must be the factor which determines whether a concrete will gain or lose water under any particular storage condition, it is reasonable to believe that the internal relative humidity will determine whether a concrete will shrink or expand under any particular storage condition, and also whether or not it is safe to apply paint or linoleum to the concrete surface. Furthermore, a measure of the relative humidity over cement pastes should give information concerning the physicochemical changes which take place during the setting and hardening of portland cement.

Spenser [1] recognized the importance of the relative humidity in concrete and attempted to measure it, but he was not successful because of the deterioration of the hair hygrometer used. Just before the present investigation was begun, F. W. Dunmore, of this Bureau, published his first report [5] dealing with the development of an electric hygrometer. It was therefore decided to investigate the possibilities of using this new hygrometer to measure the relative humidity inside concrete.

II. DESCRIPTION OF HYGROMETER

The development and construction of the electric hygrometer have been described in detail [5, 6]. The instrument consists essentially of two separate wire helices wound on a small tube which is thinly coated with a hygroscopic material, see figure 1. The electrical resistance between the two wires is a function of the relative humidity

of the air surrounding the hygrometer. Calibration curves showing the relation between electrical resistance and relative humidity are given in figure 2.

In the improved hygrometers described in reference [6], palladium wire is wound on polystyrene resin tubes. The hygroscopic coating is partially hydrolyzed polyvinyl acetate containing different percentages of lithium chloride, depending upon the humidity range for which the hygrometer is intended. This combination of materials produces a unit which is both very sensitive and very rapid in response. The rapid response of these electric hygrometers, as compared with the lagging response of hair hygrometers, is one of the factors which led to the adoption of the former for radio-sonde work.

The units developed for radio-sonde work were designed for a range of 10- to 90-percent relative humidity. Inside newly poured concrete the relative humidity is 100 percent, and considerable water may be lost before the relative humidity falls below 90 percent. Therefore, hygrometer units had to be constructed for this range. A satisfactory hygrometer was obtained by coating the unit with a very dilute polyvinyl acetate solution (containing no LiCl) and by using polystyrene washers as binding posts, instead of the Bakelite washers, which were found to become conducting when stored at high humidities.

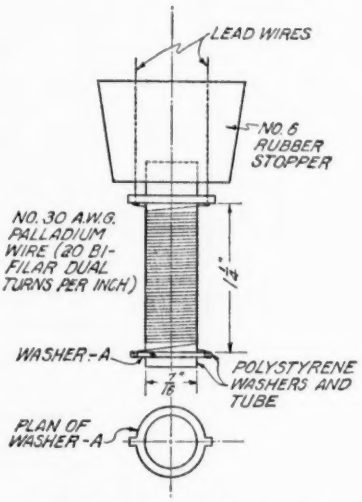


FIGURE 1.—*Electric hygrometer.*

The hygrometer units were calibrated over saturated salt solutions producing known relative humidities. The salt solutions were kept in 8-ounce glass bottles taking No. 6 rubber stoppers. In order to calibrate a unit at a given humidity, it was placed in a bottle maintained at that relative humidity, the stopper to which the unit was attached being used to close the bottle. Tables giving the relative humidity or vapor pressure produced by saturated solutions of various salts may be found in most handbooks and in the International Critical Tables.

The resistance of the units was measured with a Weston model 764 "capacity meter" calibrated to read in ohms.

III. SCOPE OF TESTS

The relative humidity at different depths (as indicated in fig. 3) inside 12-inch concrete cubes treated and stored as described in table 1 were observed over a period of 300 days. Similar observations were made in 6- by 12-inch concrete cylinders stored in tin molds with tops removed. The relative humidity inside hermetically sealed 6- by 12-inch concrete cylinders was observed at temperatures varying from 60° to 100° F. The relative humidity over hermetically sealed neat-cement pastes of approximately normal consistency was observed from the time of mixing until the pastes had aged 28 days.

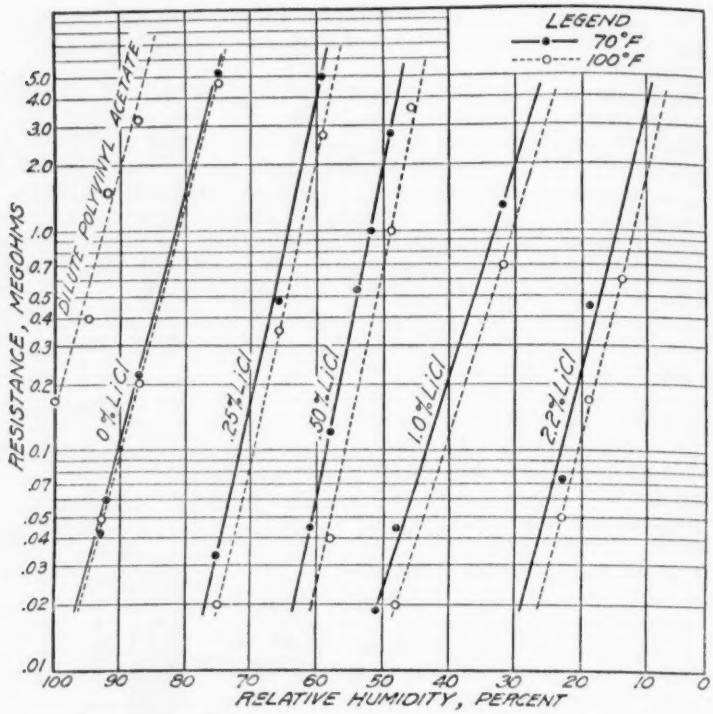


FIGURE 2.—*Calibration curves for electric hygrometers.*

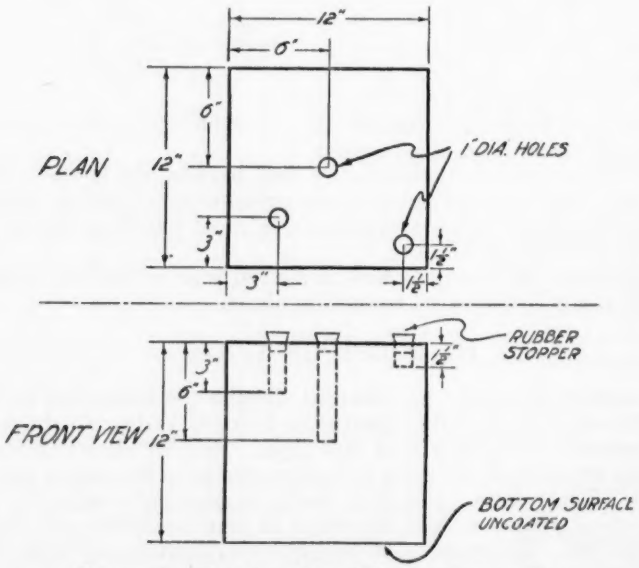


FIGURE 3.—*Location of test holes in concrete cubes.*

IV. TESTS

1. RELATIVE HUMIDITY WITHIN CONCRETE EXPOSED TO DRYING

Sixteen 12-inch concrete cubes were made, all from a 1:3:6 mix, C/W by weight=1.55. Each specimen was cast with holes, as indicated in figure 3. These holes were made by inserting 1-inch steel rods into the concrete as soon as the form was filled and pulling out the rods after approximately 20 hours. After the rods were withdrawn, the holes were closed tightly with rubber stoppers. Eight of the cubes were stored for 28 days and the other eight for 4 days, in a damp-room. At the end of these storage periods four cubes of each set were coated on five sides, as indicated in table 1, the uncoated side in each case being opposite the side containing the holes. The cubes were then placed in one of two drying rooms, one room being maintained at 100° ±2°F and 50 ±10-percent relative humidity, and the other room at 100° ±1° F and 20 ±10-percent relative humidity. By this scheme four pairs of cubes having the histories outlined in table 1 were stored in each of the two rooms.

TABLE 1.—*History of 12-inch concrete cubes*

Specimen	Damp-curing period	Coating (applied immediately after damp-curing period)	Storage after damp-curing period
	Days		
A1a	28	Not coated	50-percent relative-humidity room.
A1b	28	do	Do.
A2a	28	1 coat of asphalt emulsion, 1 thick coat of paraffin.	Do.
A2b	28	do	Do.
A3a	4	Not coated	Do.
A3b	4	do	Do.
A4a	4	2 coats of asphalt emulsion	Do.
A4b	4	do	Do.
B1a	28	Not coated	20-percent relative-humidity room.
B1b	28	do	Do.
B2a	28	1 coat of asphalt emulsion, 1 thin coat of paraffin.	Do.
B2b	28	do	Do.
B3a	4	Not coated	Do.
B3b	4	do	Do.
B4a	4	1 coat of asphalt emulsion, 1 thin coat of paraffin.	Do.
B4b	4	do	Do.

The thick paraffin coating on pair *A2* became soft at 100° F, and this made the specimens very difficult to handle. Pair *A4* was therefore given two asphalt coatings and no paraffin coating. However, the asphalt coatings were not very effective and therefore pair *B2* and pair *B4* were given one coat of asphalt emulsion plus a thin coat of paraffin.

After the cubes were placed in the drying rooms, they were weighed and the relative humidity inside the holes measured at frequent intervals. In making humidity determinations, the stopper was removed from the hole in the concrete and a stopper with attached hygrometer unit placed as quickly as possible in the hole and forced in tightly. When, in this operation, the hole was left open for 5 minutes the humidity reading was at first low, but within 30 minutes was as high as before the hole was opened. The results obtained in these tests are given in figures 4 to 13.

Figures 4 and 5 give the average loss in weight of each pair of cubes.

There is an apparent anomaly in that the specimens stored at 50-percent relative humidity, in some cases, lost more weight than the specimens stored at 20-percent relative humidity. However, pairs *A4* and *B4*, in which this anomaly was most pronounced, were given

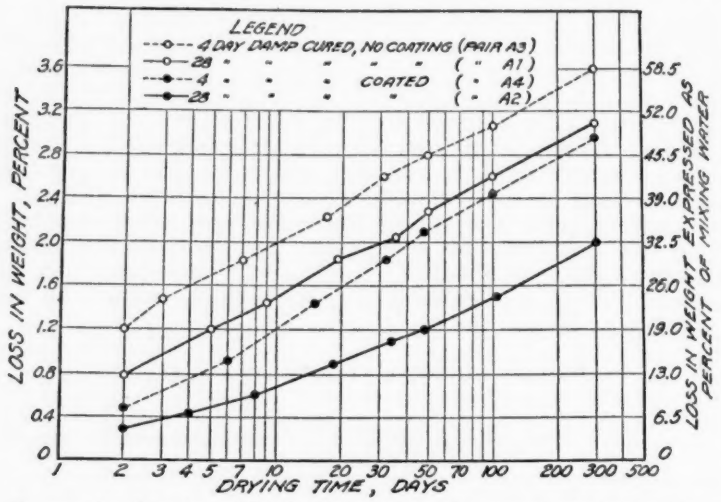

LEGEND
4 DAY DAMP CURED, NO COATING (PAIR A3)
28 " " " " " (" A1)
4 " " " COATED (" A4)
28 " " " " (" A2)
LOSS IN WEIGHT, PERCENT
LOSS IN WEIGHT EXPRESSED AS PERCENT OF MIXING WATER
DRYING TIME, DAYS
0 0.4 0.8 1.2 1.6 2.0 2.4 2.8 3.2 3.6
0 6.5 13.0 19.0 26.0 32.5 39.0 45.5 52.0 58.5
1 2 3 4 5 7 10 20 30 50 70 100 200 300 500

FIGURE 4.—*Loss in weight of cubes; stored at 50-percent relative humidity.*

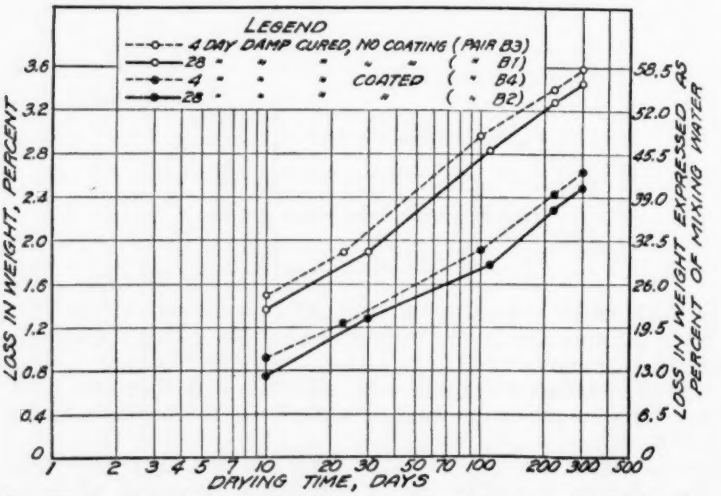

LEGEND
4 DAY DAMP CURED, NO COATING (PAIR B3)
28 " " " " " (" B1)
4 " " " COATED (" B4)
28 " " " " (" B2)
LOSS IN WEIGHT, PERCENT
LOSS IN WEIGHT EXPRESSED AS PERCENT OF MIXING WATER
DRYING TIME, DAYS
0 0.4 0.8 1.2 1.6 2.0 2.4 2.8 3.2 3.6
0 6.5 13.0 19.5 26.0 32.5 39.0 45.5 52.0 58.5
1 2 3 4 5 7 10 20 30 50 70 100 200 300 500

FIGURE 5.—*Loss in weight of cubes; stored at 20-percent relative humidity.*

different coatings. Furthermore, the 20-percent relative humidity room was much smaller than the 50-percent relative humidity room and, consequently, there may have been less circulation of air about the specimens in the former room. All specimens continued to lose weight throughout the entire 300 days of storage. However, in every case one-half the water lost in 300 days was lost the first 30 days.

The relative humidities observed in the uncoated specimens are given in figures 6, 7, 8, and 9. These figures show that even after 300 days the relative humidity in the deeper holes is still fairly high but is continuing to decrease. Except for pairs *A2* and *A4*, which

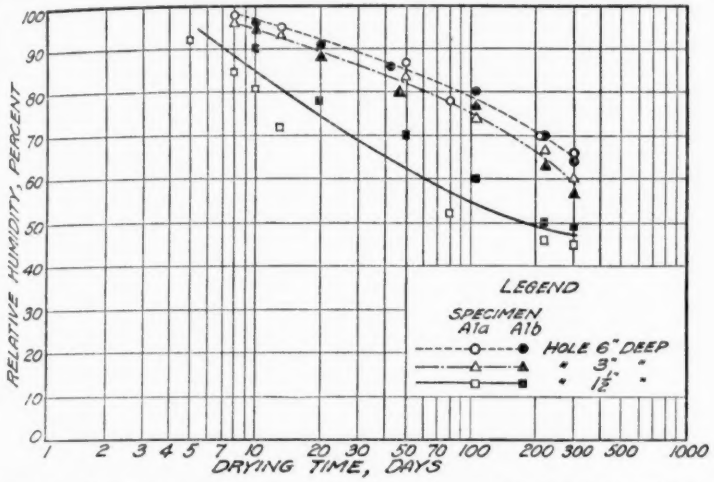


FIGURE 6.—*Relative humidity in uncoated specimens damp-cured 28 days, then stored at 50-percent relative humidity, 100° F (pair A1).*

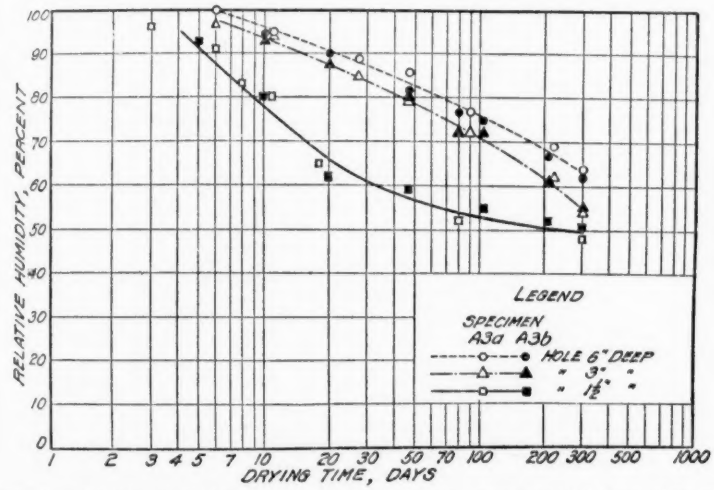


FIGURE 7.—*Relative humidity in uncoated specimens damp-cured 4 days, then stored at 50-percent relative humidity, 100° F (pair A3).*

have different types of coatings, there is no significant difference between the relative humidities in the four-day damp-cured specimens and those in the 28-day damp-cured specimens; however, figures 4 and 5 show that (except for pairs *A2* and *A4*) after 10 days' drying time the weight lost by the 4-day damp-cured specimens exceeded

by a constant amount the weight lost by the 28-day damp-cured specimens. This indicates that the excess water lost by the 4-day damp-cured specimens during the first 10 days' drying time must have been water in excess of that required for producing 100-percent

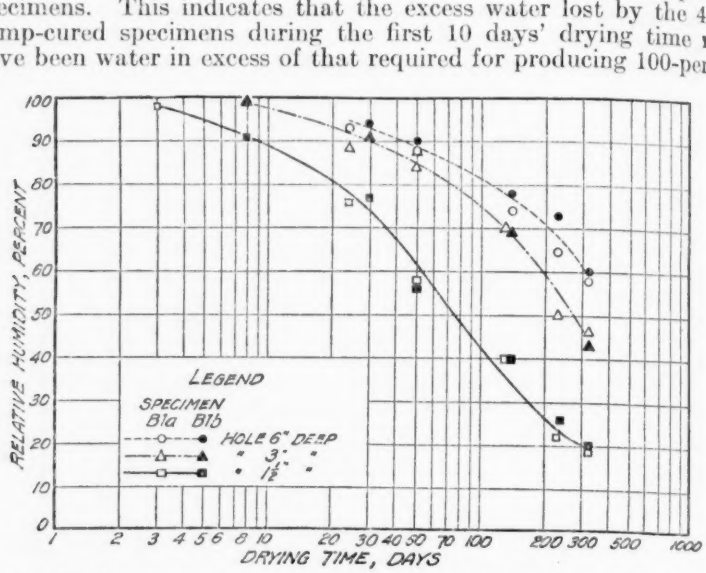


FIGURE 8.—*Relative humidity in uncoated specimens damp-cured 28 days, then stored at 20-percent relative humidity, 100° F (pair B1).*

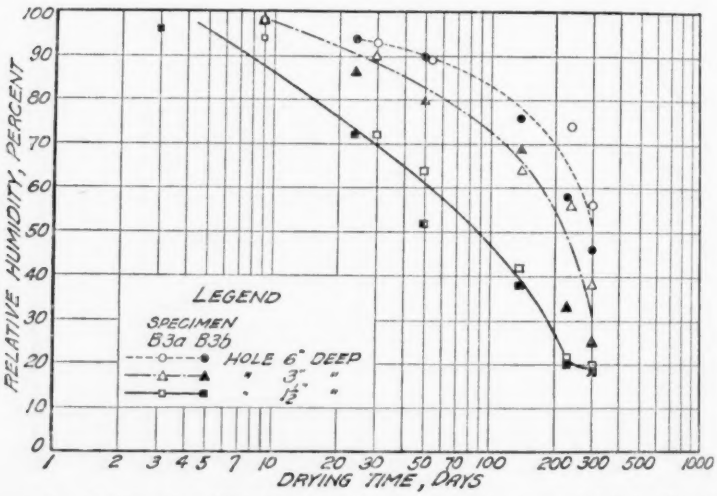


FIGURE 9.—*Relative humidity in uncoated specimens damp-cured 4 days, then stored at 20-percent relative humidity, 100° F (pair B3).*

relative humidity in the concrete. This excess water was lost very quickly in the drying room, after which the 4- and 28-day damp-cured specimens dried at equal rates.

The greatest difference between the humidity in specimens stored at 50-percent relative humidity and that in specimens stored at 20-percent relative humidity is in the 1½-inch holes, where the humidity

approached that of the storage room in each case. At any particular time the humidity in the deeper holes was about the same for the two conditions of storage. This emphasizes the fact that the interior of concrete dries very slowly, even under very dry storage conditions.

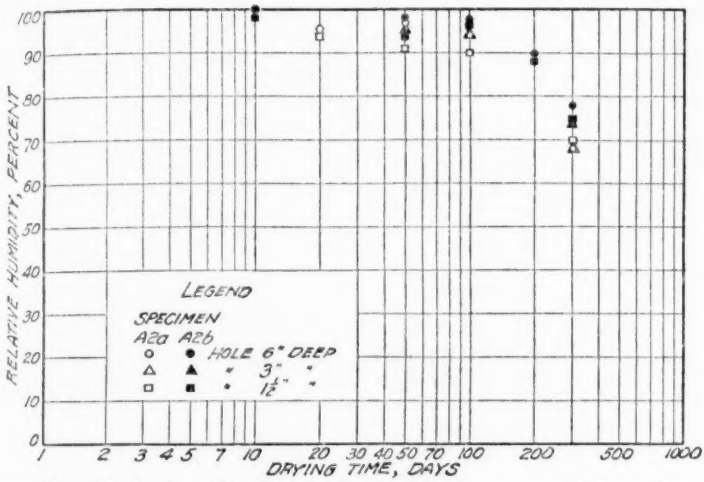


FIGURE 10.—*Relative humidity in coated specimens damp-cured 28 days, then stored at 50-percent relative humidity, 100° F (pair A2).*

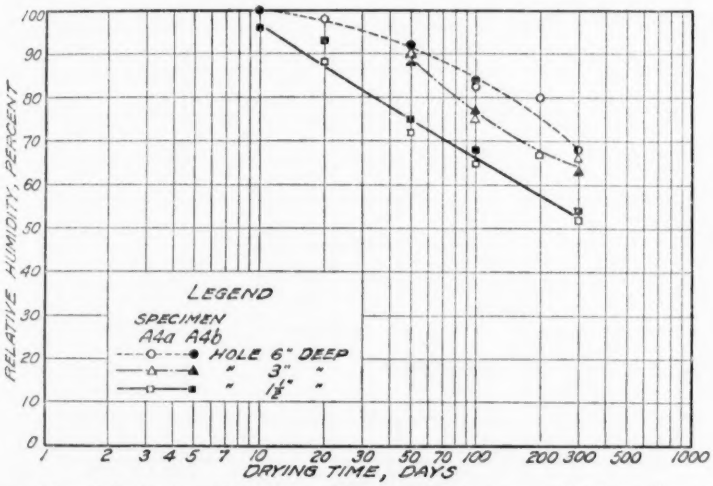


FIGURE 11.—*Relative humidity in coated specimens damp-cured 4 days, then stored at 50-percent relative humidity, 100° F (pair A4).*

Figures 10, 11, 12, and 13 give the relative humidities observed in the coated specimens. It is apparent from these figures that all of the coatings were somewhat pervious to water vapor, because, if all water lost had escaped from the uncoated side, then the 6-inch-deep holes, being nearest the uncoated side, should have been at a lower relative humidity than the 3-inch-deep or 1½-inch-deep holes. In every pair, except *A2*, the shallow holes became much drier than the deeper holes,

and this was the pair with a very thick coat of paraffin. Small broken blisters were observed in the coatings of pairs *A4*, *B2*, and *B4*. Apparently the thick paraffin coating was the only coating which was very effective in preventing loss of water.

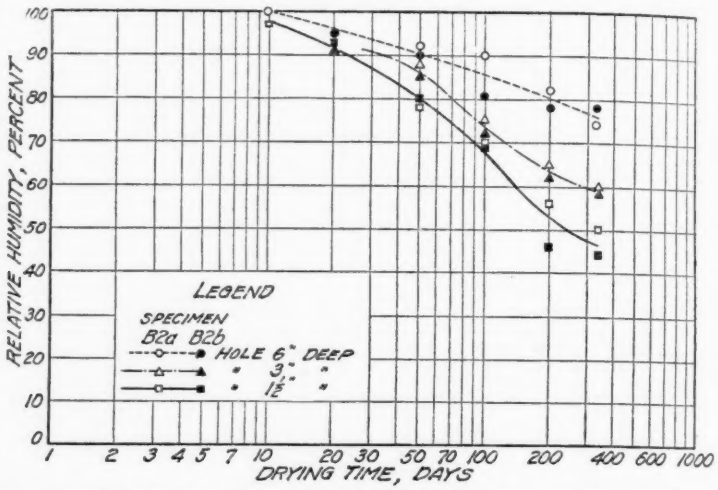


FIGURE 12.—*Relative humidity in coated specimens damp-cured 28 days, then stored at 20-percent relative humidity, 100° F (pair B2).*

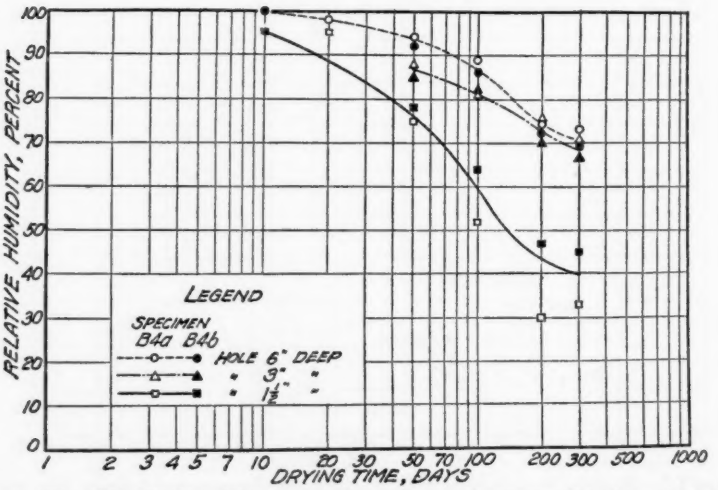


FIGURE 13.—*Relative humidity in coated specimens damp-cured 4 days, then stored at 20-percent relative humidity, 100° F (pair B4).*

In order to obtain specimens which were better sealed on all but one side, three (6- by 12-inch) concrete cylinders were cast in tin molds and kept in these molds for the duration of the test.

Each specimen was cast with a 1-inch-diameter hole in the top. These holes were 1½ inches deep in specimen 1, 3 inches deep in specimen 2, and 6 inches deep in specimen 3. The 3-inch and 6-inch holes in

these specimens were lined to within an inch of the bottom with brass tubing inserted at the time of molding. After 7 days, the tops of the molds were removed and the specimens stored in the 100° F, 50-percent relative humidity room. Relative-humidity measurements on these specimens are presented in table 2.

TABLE 2.—*Relative humidity inside 6- by 12-inch cylinders stored at 50-percent relative humidity, 100° F*

Drying time	Relative humidity		
	1½-inch hole	3-inch hole	6-inch hole
Days	*Percent*	*Percent*	*Percent*
30	78	96	98
100	60	89	91
300	57	86	88

The results show a wide spread between the humidity near the surface and the humidity near the center of the specimen, as would be expected if all water loss had to take place from the top of the specimen.

2. RELATIVE HUMIDITY INSIDE HERMETICALLY SEALED SPECIMENS

(a) EFFECT OF TEMPERATURE

In order to determine the effect of change in temperature upon the relative humidity inside concrete with a fixed water content, the tops of the three cylinders used in the above tests were covered with metal caps and the cylinders brought to temperatures of 70° and 60° F and then back to 100° F, and the relative humidity was measured at each temperature. The results are given in table 3.

TABLE 3.—*Relative humidity inside hermetically sealed concrete at different temperatures* [1]

Temperature	Relative humidity		
	1½-inch hole	3-inch hole	6-inch hole
°*F*	*Percent*	*Percent*	*Percent*
100	57	86	88
70	52	78	87
60	50	73	79
100	58	83	88

[1] The above cycle was repeated after 2 weeks' time without any appreciable difference in results.

The results show that the relative humidity decreases as the temperature decreases and that the change is reversible. It is worthy of note that this relation between relative humidity and temperature is opposite to the relation that would hold if sorption phenomena were absent, that is, if concrete consisted of noncolloidal material containing large pores filled with air and water vapor (no liquid water). In this case, if the temperature were decreased, the relative humidity of the air in the large pores would increase until the dew point, or 100-percent relative humidity, was reached. On the other hand, when sorption is pronounced, as in colloidal structure or porous materials with large

surface (small pores), the relative humidity may decrease as the temperature decreases. This phenomenon has been reported in the case of wools [7], and it is indirectly shown to hold for silica gel by the data of Patrick [8].

(b) EFFECT OF SETTING AND HARDENING OF CEMENT PASTE

A series of tests was made in which the electric hygrometer was used to measure the relative humidity over cement pastes as the pastes aged. In these tests approximately 500 g of freshly mixed cement paste was placed in an 8-ounce glass bottle and the bottle immediately sealed with a rubber stopper and polystyrene cement. The bottles were then stored at 70° F and the relative humidity in the bottle was measured at different ages, the rubber stopper being removed and replaced with another stopper to which an electric hygrometer was attached. Preliminary work was done to assure that the method of sealing the bottles was efficient and to determine the effect of opening the bottle at each measurement. Specimens sealed in bottles and stored in the moist cabinet gave results which agreed with those obtained on similarly sealed specimens stored in the laboratory, nor could any change in weight be detected in either set with an analytical balance. A specimen in a bottle which had a hygrometer sealed in it throughout the test gave results which checked with those obtained by the usual method, in which the bottle was opened for each measurement. The results given in table 4, therefore, represent values for specimens which neither gained nor lost water during aging.

TABLE 4.—*Relative humidity over neat paste stored in hermetically sealed bottles*

Age (days)	High-early-strength cement, plus the following percentages of H_2O—[Normal consistency, 27% of H_2O]			
	23% of H_2O	24% of H_2O	25% of H_2O	27% of H_2O
	%	%	%	%
2	87	(a)	88	(a)
3	82	(a)	86	88
4	(a)	82	84	86
5	79	80	84	84
7	78	79	82	82
14	76	(a)	(a)	81
21	(a)	76	(a)	(a)
37	75	(a)	80	80
	Moderate heat-of-hardening cement, plus the following percentages of H_2O—[Normal consistency, 22% of H_2O]			
	17% of H_2O	22% of H_2O	27% of H_2O	32% of H_2O
1	96	(a)	(a)	(a)
2	92	95	(a)	(a)
3	90	94	97	(a)
4	90	94	97	(a)
7	88	94	(a)	(a)
15	87	97	(a)	100
28	86	88	(a)	97

(a) No determination made.

These results show (1) the variation in relative humidity with time and with small changes in amount of mixing water, and (2) the difference in relative humidity over pastes made from two widely differing cements. An apparent relation between strength and reduction in relative humidity is indicated by the fact that the briquette strength and the relative humidity for the high-early-strength cement aged 3 days were respectively the same as the strength and relative humidity for the moderate heat cement aged 28 days.

V. ACCURACY OF METHOD

The accuracy with which the relative humidity inside concrete can be determined with the electric hygrometer depends, to some extent, upon the care with which the calibration is checked at the time the relative humidity is measured. The first instruments which were used changed in calibration with time, and in order to obtain an accuracy of ± 2 percent it was necessary to check the calibration at least once a week. With the latest type unit this is not necessary. However, in very precise work, such as the determination of the relative humidity over hermetically sealed cement pastes, the hygrometer, when not in use, may be kept in a bottle at a known relative humidity and corrections made for any change in calibration. Such corrections are seldom greater than 2 percent relative humidity and are practically constant over the entire range of the hygrometer, that is, a calibration curve, as shown in figure 2, is shifted to the right or left without changing slope. It is therefore necessary to check the calibration at one point only. By this method an accuracy of ± 1-percent relative humidity may be obtained.

VI. SUMMARY AND CONCLUSIONS

1. The importance of the relative humidity inside concrete is pointed out, and the bearing which it may have on certain physical properties is suggested.

2. The electric hygrometer developed at the National Bureau of Standards for radio-sonde use is described, and a method is given for using this hygrometer to measure the relative humidity inside cavities within concrete.

3. Measurements of the relative humidity inside 12-inch concrete cubes were made over a period of 300 days. The relative humidities inside uncoated specimens was as follows:

Drying time	Relative humidity of drying room	Relative humidity inside concrete	
		1½-inch hole	6-inch hole
Days	*Percent*	*Percent*	*Percent*
50	50	70	92
300	50	50	66
50	20	52	90
300	20	20	60

The relative humidity inside coated specimens was higher than in the uncoated specimens, but the results indicated that none of the coatings were impermeable to water.

4. The relative humidity inside hermetically sealed concrete specimens was found to decrease as the temperature decreased and to return to its original value when the temperature was increased to its original value.

5. The relative humidity over neat-cement pastes of approximately normal consistency and cured in hermetically sealed containers was measured. The relative humidity decreased to 94 percent at 7 days and to 88 percent at 28 days, over a moderate heat-of-hardening cement, and decreased to 88 percent at 3 days, to 82 percent at 7 days, and to 79 percent at 28 days, over a high-early-strength cement.

6. The electric hygrometer appears to be well suited to the measurement of relative humidity inside concrete and over cement pastes.

The authors express their appreciation to F. W. Dunmore for supplying the necessary hygrometers and for his valuable suggestions as to their use.

VII. REFERENCES

[1] R. W. Spenser, Proc. Am. Concrete Inst. **34,** 45 (1938).
[2] R. E. Davis and G. E. Troxell, Proc. Am. Concrete Inst. **25,** 210 (1929).
[3] L. Jesser, Zement **16,** 741 (1927); **18,** 158 (1929).
[4] R. K. Schofield, Trans. Third International Congr. Soil Sci. **2,** (1935).
[5] F. W. Dunmore, J. Research NBS **20,** 723 (1938) RP1102.
[6] F. W. Dunmore, J. Research NBS **23,** 701 (1939) RP1265.
[7] J. W. McBain, *The Sorption of Gases and Vapours by Solids* (Routledge & Sons, London).
[8] W. A. Patrick, P. B. Davis, and E. H. Barclay, Colloid Symposium Annual, **7,** 131, 1930. (Johns Hopkins, 1929.)

WASHINGTON, June 22, 1940.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1335

Part of Journal of Research of the National Bureau of Standards, Volume 25, October 1940

NOTE ON THE EFFECTS OF COBALT AND NICKEL IN STORAGE BATTERIES

By George W. Vinal, D. Norman Craig, and Clarence L. Snyder

ABSTRACT

The presence of small amounts of cobalt or nickel sulfates in the electrolyte of storage batteries decreases the charging voltages. Iron sulfate was included in the study also, because of its chemical similarity to the others. As a result of 150 cycles of charge and discharge of a group of commercial storage batteries, it was found (1) that cobalt decreases the charging potential of positive plates but has a destructive action on the separators, (2) nickel decreases the charging potentials of negative plates without apparent harmful effect on the separators, and (3) iron has little if any effect on the potentials of either positive or negative plates. Advantages that might be gained by the use of cobalt, if the difficulty with separators is overcome, are indicated.

The cause of hydrogen evolution from storage batteries when not on charge was the subject of a paper by the authors [1] several years ago. In that paper, as well as in other publications which are discussed there, it is evident that antimony liberated by corrosion of positive plates deposits on the negative plates and is a cause of local action which is accompanied by the liberation of gaseous hydrogen. The most obvious means of avoiding this would be the elimination of antimony from the battery, but no substitute for the lead-antimony alloy has found general use, although a number of substitute alloys have been proposed.

In general, lead alloys which are free from antimony result in charging voltages which are higher than those ordinarily observed. This fact has been cited by some engineers as the reason that substitute alloys often corrode more than the customary lead-antimony alloys. If the higher charging voltages were the cause of increased corrosion of the positive plates, the difficulty of finding a suitable substitute for lead-antimony alloys would be seriously increased. In the publication mentioned above, it was shown that the increased charging voltages in cells without antimony are caused by differences in the potentials of the negative plates, while the positive plate potentials remain substantially the same as in an ordinary cell. Positive grids without antimony, therefore, are not subject to more corroding conditions.

Other methods of attacking the problem of spontaneous hydrogen evolution include the search for a stable compound which would withstand cycling in a battery and yet inhibit the liberation of gaseous hydrogen when the battery is discharging or idle. Although

[1] G. W. Vinal, D. N. Craig, and C. L. Snyder, BS J. Research **10**, 795 (1933) RP567.

a number of inhibitors have been tried, the results obtained at the Bureau up to the present time have not been particularly successful. Search for a means of decreasing the charging potentials of the positive plates has been more encouraging, but much experimental work remains to be done. Our experiments were interrupted in July 1939. It seems worth while to make a preliminary report now, as the completion of the next phase of the work will require considerable time.

A paper [2] entitled "The behavior of lead anodes in a sulfate electrolyte with particular reference to the influence of cobalt salts"

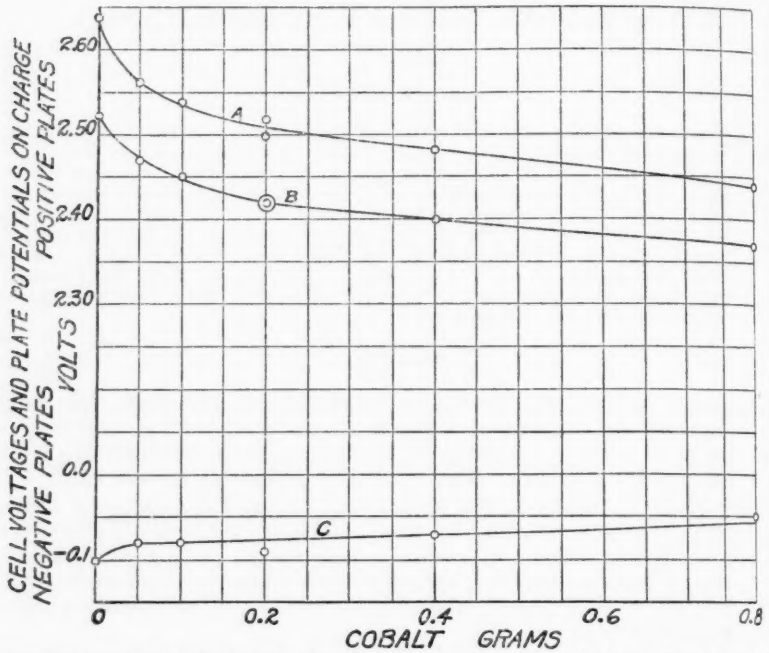


FIGURE 1.—*Effect of cobalt on the cell voltage and on the cadmium potentials of the positive and negative plates.*

Curve *A*, cell voltage; curve *B*, positive-plate potential; curve *C*, negative-plate potential

reports decreased corrosion of lead anodes when a cobalt salt is present. This paper is not concerned with storage batteries, and no potential measurements on positive plates are given. A paper by Fink [3] discusses the catalytic properties of cobalt.

In our study of the effect of cobalt in a storage battery, various amounts of cobalt sulfate were added to the electrolyte. Previous experiments had shown that nickel also had an effect on charging voltages. Because of the relationship of iron to nickel and cobalt, all three of these were tested similarly. Comparisons were made with other cells to which none of these materials was added.

The experiments consisted in cycling small storage cells of the automotive type. These were of commercial manufacture. Each cell had a rated capacity of 45 ampere-hours and contained nine plates with wood separators. These cells were presumed to be sufficiently alike for the purposes of the experiment. In all, about 150

[2] M. Rey, P. Coheur, and H. Herbiet, Trans. Electrochem. Soc. 73, 315 (1938).
[3] C. G. Fink, Trans. Electrochem. Soc. 71, 491 (1937).

cycles of charge and discharge were made. Two discharges of 4 hours and two charges of 8 hours were made in each 24-hour period.

The results of the experiments are given in table 1. The effect of cobalt in reducing the potential of the positive plates is shown in figure 1. The change in potential of these plates with increasing amounts of cobalt is large compared to the relatively insignificant changes that occurred in the potentials of negative plates. Cobalt, however, seriously affected the separators. In this respect it is like manganese, which affects both wood and rubber separators. It is probable that cobalt would affect rubber also. Some of the positive

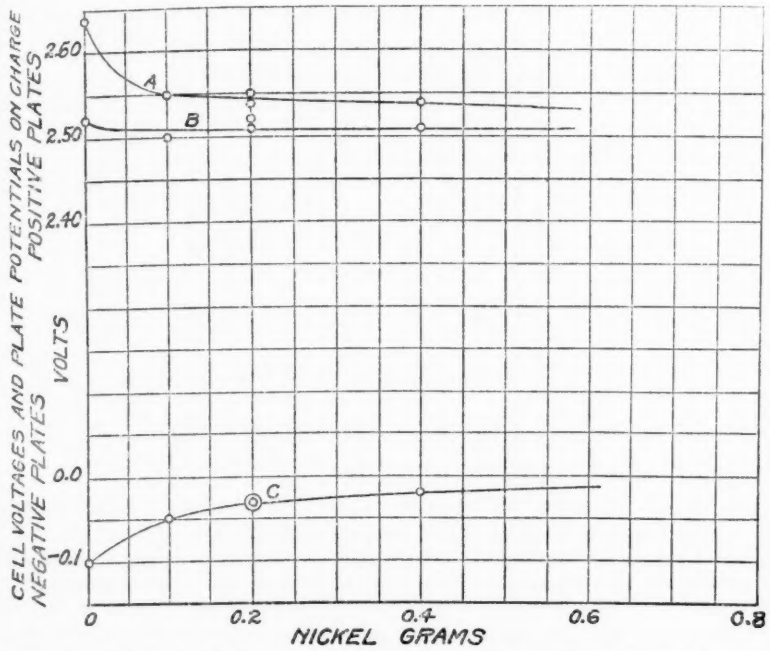


FIGURE 2.—*Effect of nickel on the cell voltage and on the cadmium potentials of the positive and negative plates.*

Curve *A*, cell voltage; curve *B*, positive-plate potential; curve *C*, negative-plate potential.

plates, particularly those in the cells having the highest amounts of cobalt, were in distinctly better condition at the end of the experiment than those in the blank cells.

Nickel affects the cadmium voltages of the negative plates and appears to be without specific action on the positives (see fig. 2). Separators in these cells were unaffected. When both cobalt and nickel were added to the cells, their effects were additive and independent of each other. The separators were, however, affected by the cobalt.

Iron has no specific effect on the potentials of either positive or negative plates. Its deleterious effects in storage batteries are well known and require no discussion here.

TABLE 1.—*Effect of materials added to the electrolyte*

[Cobalt sulfate, $CoSO_4.7H_2O$; nickel sulfate, $NiSO_4.7H_2O$; ferrous sulfate, $FeSO_4.7H_2O$]

Material		Voltages, initial tests			Voltages, after 150 cycles			Remarks
Name	Amount added	Cell	(+)Cd	(−)Cd	Cell	(+)Cd	(−)Cd	
	g	*v*	*v*	*v*	*v*	*v*	*v*	
None		2.64	2.52	−0.11	2.62	2.57	−0.4	Mean of 10 control cells; positives soft; some shedding.
$CoSO_4.7H_2O$	0.25	2.56	2.47	−.08	2.51	2.52	+.01	Separators perforated after 150 cycles.
Do	.5	2.54	2.45	−.08	2.42	2.45	+.03	Do.
Do	1.0	2.52	2.42	−.08	2.27	2.35	+.07	Do.
Do	1.0	2.50	2.42	−.09	2.32	2.42	+.10	Do.
Do	2.0	2.48	2.40	−.07	2.33	2.36	+.02	Do.
Do	4.0	2.44	2.37	−.05	2.45	2.38	−.07	Separators thin but not perforated; positives firm; no shedding.
$NiSO_4.7H_2O$	0.5	2.55	2.50	−.05	2.53	2.54	+.01	Separators good; positives soft and shedding.
Do	1.0	2.54	2.51	−.03	2.53	2.56	+.03	Do.
Do	1.0	2.55	2.52	−.03	2.54	2.54	.00	Do.
Do	2.0	2.54	2.51	−.02	2.50	2.55	+.05	Do.
$CoSO_4.7H_2O$, $NiSO_4.7H_2O$, each.	0.25	2.52	2.47	−.05	2.54	2.54	.00	Separators thin; positives shedding.
Do	.5	2.48	2.44	−.04	2.35	2.42	+.08	
Do	.5	2.48	2.44	−.03	2.37	2.44	+.07	
Do	1.0	2.44	2.41	−.03	2.26	2.34	+.08	
$FeSO_4.7H_2O$	0.5	2.63	2.52	−.11	2.64	2.59	−.04	
Do	1.0	2.64	2.52	−.12	2.68	2.59	−.09	Separators good, positives soft, and washed out.
Do	1.0	2.65	2.51	−.13	2.66	2.58	−.08	
Do	2.0	2.64	2.51	−.12	2.64	2.56	−.09	

Decreased charging voltages are desirable because (1) excess voltages on auxiliary apparatus can be avoided, (2) the voltage efficiency of the battery is increased. Notwithstanding the deleterious effects of cobalt on the separators, the importance of its specific property of decreasing the polarization of the positive plates warrants further investigation because decreased positive plate potentials may permit the use of lead alloys other than those containing antimony. The remaining problem is the protection of the separators. It may be possible to overcome this difficulty by the use of glass mats, but our experiments up to the present have not included this phase of the work.

In conclusion, the three related elements, iron, cobalt, and nickel, produce markedly different effects in a storage battery. Cobalt reduces the polarization of the positive plates, and nickel reduces the polarization of the negative plates. Iron, on the other hand, does not appear to affect the potential of either positives or negatives by a significant amount. Cobalt apparently decreased the corrosion of the positives but had a deleterious action on the separators.

WASHINGTON, July 31, 1940.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1336

Part of Journal of Research of the National Bureau of Standards, Volume 25, October 1940

MEASUREMENT OF ELECTRODE POTENTIALS AND POLARIZATION IN SOIL-CORROSION CELLS

By Robert B. Darnielle

ABSTRACT

Electrode potentials in soil-corrosion cells cannot be measured accurately by the direct method because of the high resistance of soils and because of the nature of the electrolyte and the electrodes. Measurements made with a mechanical interrupter are also in error because of depolarization during the period of interruption. The method described by Hickling was adapted to measurements of these cells. The method was found to be accurate to about 0.01 volt over the range of current, resistance, and rate of depolarization of soil-corrosion cells.

CONTENTS

	Page
I. Introduction	421
II. Problem of measuring electrode potentials in soil-corrosion cells	422
1. Description of cell	422
2. Measurement of single-electrode potentials	422
3. Measurement of potential difference between the anode and cathode	424
III. Measurement of potentials by the Hickling method	425
1. Description of the method	425
2. Values of potential for different periods of interruption	428
IV. Measurement of potentials by means of alternating current with elimination of *IR* drop	429
V. Measurement of potential difference between the anode and cathode	430
VI. Comparison of potential measurements by different methods	431
VII. References	433

I. INTRODUCTION

Rates of corrosion of steel in soils have been shown to be indicated by the relation between current and electrode potentials in corrosion cells in which current flows without applied emf [1].[1] Recently it has been shown that the current required to polarize the electrodes of the corrosion cell to the same potential in the absence of *IR* drop may be taken as a measure of the rate of corrosion of steel in soils [2]. This current is equal to the short-circuit current which would flow if the cell had no resistance, and corresponds to the current in a natural corrosion circuit in which the electrodes are very close together. The electrode potential corresponding to this current has been termed "the corrosion potential."

Apart from the value of the current-potential relations in measuring corrosion rates, these relations are useful as a means for investigating the mechanism of the corrosion reaction in soils. In particular, such curves have been employed in determining the electrode at which the

[1] Figures in brackets indicate literature references at the end of this paper.

corrosion rate is chiefly controlled under various soil conditions [2]. Although measurement of the potentials of polarized electrodes of a variety of materials can be made with accuracy in certain solutions, it will be shown that the usual methods are not applicable to measurements in soil-corrosion cells.

II. PROBLEM OF MEASURING ELECTRODE POTENTIALS IN SOIL-CORROSION CELLS

1. DESCRIPTION OF CELL

The cell used in this investigation has been described by the writer and his associates. However, a brief description is presented herewith [2]. The anode of the cell is a disk separated from the screen cathode by a layer of moist soil, the whole being contained within a Bakelite ring (fig. 1). As the screen is more accessible to air than the disk, to which direct access of air is prevented by a layer of paraffin, the screen assumes a more noble potential. As a result, current flows within the cell from the disk to the screen when the electrodes are connected externally. In order that the aeration of the electrodes shall be determined by the permeability of the soil to air, the screen is covered by a layer of soil of the same thickness and at the same moisture content as the soil which constitutes the electrolyte. In the present study, steel electrodes were used. Single-electrode potentials were measured with respect to a saturated calomel electrode in contact with the surface of the soil, as indicated in figure 1. The term "electrode potential," as used in this paper, refers to this type of measurement as made in the absence of IR drop.

If the short-circuit current through the cell is increased by the application of an external voltage, the electrodes may be brought to the corrosion potential, the corresponding current being taken as the measure of corrosion, as previously stated. The current-potential relation for soil-corrosion cells is illustrated in figure 2 by the solid lines. With the most corrosive soils in which the open-circuit voltage is 0.3 to 0.4 volt and the current required to bring the electrodes to the same potential is between 3 and 4 ma, it is unnecessary to extend the current-potential curves beyond the point of intersection in order to decide whether the corrosion rate is determined by the rate of the anode or the cathode reaction. With the less corrosive soils the curves are extended until the potential difference between the anode and cathode is about 0.4 volt. Potential differences between the anode and cathode to the left of the equipotential point are considered negative; those to the right of this point are positive.

2. MEASUREMENT OF SINGLE-ELECTRODE POTENTIALS

The potentials of polarized electrodes are commonly measured by the direct method, the potentials of the anode and cathode being measured with respect to a reference electrode while the polarizing current is flowing. As a potential measured under these conditions will include any potential difference required to overcome resistance, errors from this source are made as small as possible by placing the tip of the reference electrode in close contact with the electrode whose potential is being measured, or by placing the reference electrode out of the path of current flow. According to Hickling [3], the error

resulting from inclusion of some *IR* drop in the measured potential is seldom avoided, as there always is present a certain surface resistance which may be due to gas evolution, depletion of electrolyte in the layer in contact with the electrode, or, in the case of an anode, to a poorly

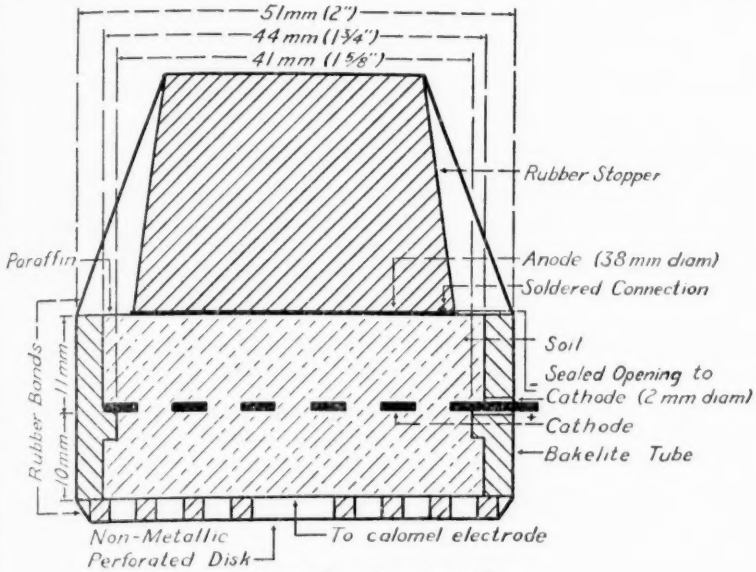


FIGURE 1.—*Corrosion cell.*

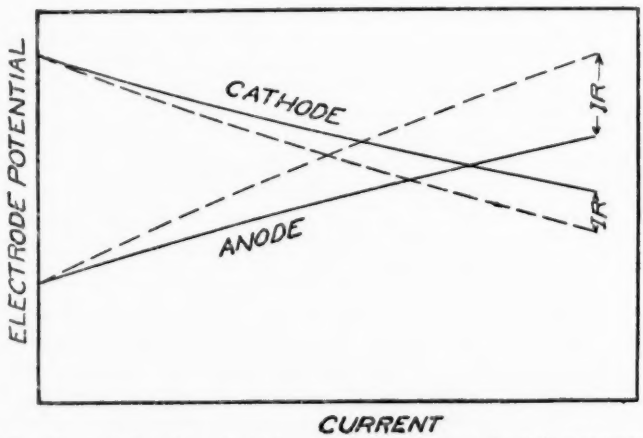


FIGURE 2.—*Current-density-potential curve, illustrating potential measurements in soil cells.*

The broken lines illustrate measurements of potentials which include *IR* drop. The current at the intersection of the solid lines is the current at the corrosion potential.

conducting oxide film. As film development or the deposition of corrosion products is characteristic of metals corroding under various conditions, it follows that in accurate measurements of electrode potentials in corroding environments, possible errors due to resistance films must be considered.

Wholly apart from any error due to the resistance of films, the high resistivity of soils renders potential measurements particularly difficult. Even if the construction of the cell would permit close contact between the tip of the reference electrode and the cell electrodes, this procedure would be objectionable because of large variations in potential which often occur on electrode surfaces.

To eliminate errors due to *IR* drop, it has been considered necessary by some to interrupt the current. This is usually accomplished by means of a mechanical interrupter, the potential being measured during the interruption [4, 5]. It is evident that the accuracy of potential measurements made with interrupted current depends upon the time elapsing between interruption of the current and measurement of the potential and the rate at which the potential is changing. According to Hickling [3], it is possible to interrupt currents for periods as short as 10^{-5} second by means of an electronic device. A second electronic circuit enables electrode potentials to be measured within this time interval.

3. MEASUREMENT OF POTENTIAL DIFFERENCE BETWEEN THE ANODE AND CATHODE

For determination of soil-corrosion rates, individual measurements of anode and cathode potentials are not necessary. As such determinations consist simply in measuring the current required to polarize the electrodes of the corrosion cell until their potentials are the same, it is evident that the particular value of the corrosion potential with reference to a standard electrode need not be known. If it were not for the high and variable resistance of many soil cells, measurement of the difference of electrode potentials, as previously defined, would consist simply in measuring the voltage of the cell at various applied currents and correcting these values for the *IR* drop, calculated from the alternating-current resistance. However, the marked changes which may occur in the resistance of corrosion cells with applied current renders the calculation of *IR* drop and the resulting value of the difference of electrode potentials subject to large errors.

During the application of current, the resistance of a soil contained between two electrodes may change at one or both electrodes and in the soil mass itself, and these changes may be in opposite directions. Measurements of potential difference between two nonpolarizing electrodes placed in the path of current (d-c) flow in a rectangular cell indicated that the resistance of a certain soil of high resistivity decreased with increasing current.[2] Measurements of the alternating-current resistance between the anode and cathode of a soil-corrosion cell indicated that the change in resistance may or may not resume its previous value after the direct current is reduced to zero.

From the considerations which have been advanced in this section, it follows that methods involving the use of continuous current are

[2] Decrease in resistance within the soil can be accounted for by assuming that some of the water in a moist soil is contained in discontinuous pores. As the potential difference across the cell is increased, the water is forced by endosmose into capillaries which, by forming continuous channels, increase the number of conducting paths and hence the conductance of the soil. A simultaneous increase in resistance between the anode and the soil would result from forcing the water away from the electrode under the influence of the endosmotic pressure and clogging of the soil pores with corrosion products. Changes in resistance identical in character with those which have been described have been reported by Evershed [6] in a study of insulation resistance. However, the resistances measured and the voltages applied by Evershed were much greater than those measured in the soil cells.

Aside from endosmotic effects, a probable cause of increased resistance at the anode is the deposition of corrosion products on the metal surface.

open to serious objection for the measurement of electrode potentials and polarization in soil cells. Methods involving the interruption of the current would be satisfactory only to the extent that the period of interruption is sufficiently short to prevent error due to depolarization. Because of the very short period of interruption produced by the electronic method of Hickling, this method was selected for investigation.

III. MEASUREMENT OF POTENTIALS BY THE HICKLING METHOD

1. DESCRIPTION OF THE METHOD

The Hickling method for measuring the potential of polarized electrodes utilizes an electronic interrupter and an electronic poten-

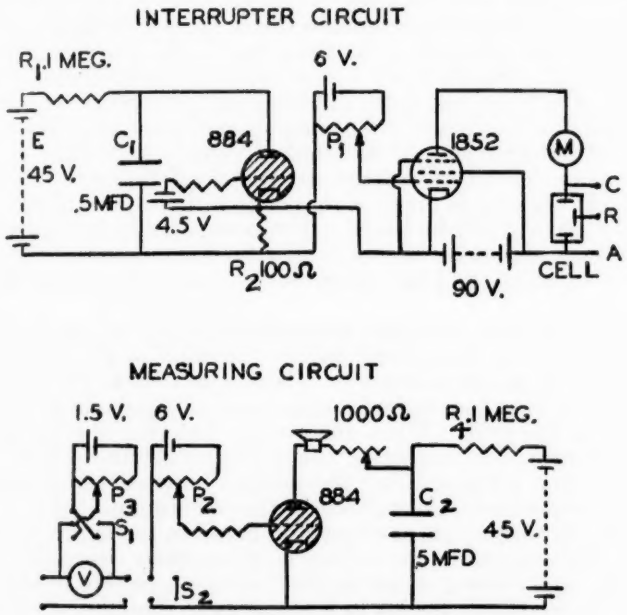


FIGURE 3.—*Circuit diagram of the Hickling method.*

tiometer, by means of which potentials can be measured a very short time after the current has been interrupted.

Figure 3 shows the essential parts of the interrupter and measuring circuit. Capacitor C_1 is charged through resistor R_1 until the plate of the thyratron (type 884) is at a certain potential, depending on the grid voltage. The tube then becomes conducting and capacitor C_1 discharges through the tube and resistor R_2 until the capacitor voltage drops to about 15 volts, when the tube becomes nonconducting, and the process is repeated at a rate depending on the values of E_1, R_1, C_1, and E_2.

The cell is in the plate circuit of the pentode (type 1852). Its current may be controlled by potentiometer P_1 and the IR drop across R_2. Each voltage pulse across R_2 imparts a large negative potential to the

grid of the vacuum tube, thereby interrupting the current in the cell. Resistors should be connected in series with the grid of each thyratron to limit grid current when the tubes conduct current.

The measuring circuit is an oscillating circuit similar to the interrupter circuit and will not oscillate when the grid of the thyratron is below a certain critical potential.

In measuring electrode potentials, the electrodes are connected to the grid circuit of a thyratron, the grid having been adjusted to the critical potential. The cell is so connected that the grid of the thyratron is most negative between interruptions of the current because of *IR* drop in the cell. When the current is interrupted, the grid potential will be above or below the critical potential by an amount equal to the potential of the electrode. Adjustment of a potentiometer in the grid circuit, so that the critical potential is restored, measures the electrode potential.

In operation, double-pole double-throw switch S_2 is closed to the right (fig. 3), and the grid of the thyratron in the measuring circuit is adjusted to the critical point by means of the potentiometer P_2, as indicated by slow ticking in the loudspeaker. By reversing switch S_2, the cell and the voltmeter-potentiometer are introduced into the grid circuit of the thyratron. If the applied voltage makes the grid more negative than the critical voltage, no sound will be heard in the loudspeaker. If the grid is made more positive than the critical voltage, very rapid ticking will be heard. Potentiometer P_3 is then adjusted until the rate of ticking is identical with the rate when the critical point was adjusted, and the potential difference is read on the voltmeter.

It is important to note that the connections of the measuring circuit to the cell are determined by the direction of *IR* drop and not by the polarity of the electrodes. Hence in measuring the voltage between the anode and cathode of the cell, the cathode of the cell is connected to the grid. When the voltage between the anode and a reference electrode is measured, the reference electrode is connected to the grid, and for measuring the voltage between the cathode and the reference electrode, the cathode of the cell is connected to the grid. A switching arrangement, not shown in detail in the figure, is used for making rapid changes in connecting to the various electrodes.

When the cell current is interrupted, it drops quickly to a very low value and immediately begins to increase as C_1 discharges. The time required for the current to decrease to a minimum and then increase until the *IR* drop is more than 0.01 volt, the approximate limit of accuracy of the measurement, may be designated as the "effective" period of interruption. This interval corresponds to the maximum time during which the electrode depolarizes before its potential is measured.

Hickling's measurements were made with high current densities in cells of very low resistance, a triode being used as the vacuum tube. In order to make the effective period of interruption independent of the polarizing current, the latter was controlled by adjusting the filament current. For measuring potentials in soil cells in which the resistance is high and the current low, the use of a sharp cutoff pentode permitted control of the plate current in the usual way, that is, by regulation of the grid voltage. By eliminating lag in the adjustment of the current in this manner, potential measurements

could be made immediately after the current was changed, which is usually desirable in measurements with soil cells. With variation of current and resistance over the extreme range used in corrosion studies, the effective time of interruption was found to be reasonably constant. However, the chief advantage of the pentode over the triode was the greatly improved accuracy of measurement obtained with the former tube. Pentodes of the types 6J7 and 1852 have a very sharp cutoff and provided sufficient plate current for potential measurements in the soil cells.

Calculation of the effective period of interruption from the parameters of the circuit indicated that this time was about 3×10^{-5} second. By the more direct method described below, the value 8×10^{-5} was obtained with R_2 equal to 75 ohms. As the value of 3×10^{-5} applies to measurements made under static conditions, which are different from the transient conditions of operation, it is likely that the value of 8×10^{-5} obtained by the second method is more nearly correct.

TABLE 1.—*Accuracy of the Hickling method for various values of current and resistance*

[Resistance in interrupter circuit=75 ohms]

Resistance in test circuit	Current	*IR*	Voltage with current interrupted
Ohms	*ma*	*v*	*v*
100	1.0	0.1	+0.01
100	2.0	.2	+.01
100	3.0	.3	.00
100	5.0	.5	.00
100	8.0	.8	.00
100	9.0	.9	−.01
100	10.0	1.0	−.01
2,000	0.5	1	.00
2,000	1.0	2	.00
2,000	2.0	4	.00
2,000	4.0	8	.00
2,000	6.0	12	.00
2,000	8.0	16	.00
4,000	0.5	2	−.01
4,000	1.0	4	−.01
4,000	2.0	8	.00
4,000	4.0	16	.00
4,000	5.0	20	+.01
4,000	6.0	24	+.01
4,000	7.0	28	+.01
4,000	7.5	30	+.02
6,000	0.5	3	−.02
6,000	1.0	6	−.01
6,000	2.0	12	−.01
6,000	3.0	18	.00
6,000	4.0	24	+.01
6,000	5.0	30	+.02
6,000	6.0	36	+.02
6,000	6.2	37.2	+.03
10,000	0.1	1	+.02
10,000	.5	5	+.02
10,000	1.0	10	+.02
10,000	2.0	20	+.02
10,000	3.0	30	+.08
10,000	4.0	40	+.10

The effective period of interruption was measured as follows. A capacitor and a resistor in parallel were connected in the circuit in place of the cell. The potential of the capacitor was measured with continuous current and with interrupted current. The first measurement gave the initial potential of the capacitor; the second, the

potential to which it discharged. The effective period of interruption was then calculated from the known values of the resistance and capacitance.

The periods of interruption given above are, of course, not comparable with those obtained by Hickling for the same value of R_2, since the period of interruption depends on factors other than R_2.

To determine the extent to which measurements of electrode potentials had been made independent of both current and resistance, various resistors were used successively in place of the cell, and the potential difference across the resistance was measured as the current was varied. The shortest time interval was used. As there is practically no IR drop when the plate current is interrupted, the potential difference should of course be zero.

The data of table 1 show that within the range of current commonly applied to soil-corrosion cells and within the normal range of resistance of these cells, the combined effect of current and resistance on the accuracy of potential measurements is not over 0.01 volt. The larger errors shown in the table correspond to higher IR drops than are met with in practice. It is to be noted that accurate measurements were made with IR drops as much as 20 volts, except with the highest resistance of 10,000 ohms.

2. VALUES OF POTENTIAL FOR DIFFERENT PERIODS OF INTERRUPTION

TABLE 2.—*Values of potential difference between the anode and cathode, and single-electrode potentials for different periods of interruption*

Soil		Current density	Resistance in interrupter circuit—ohms					
No.[1]	Type		100	200	400	600	1,000	2,000
			Potential difference between anode and cathode					
		ma/dm[2]	*v*	*v*	*v*	*v*	*v*	*v*
55	Hagerstown loam	1.8	+0.28	+0.25	+0.23	+0.22	+0.20	+0.18
113	Imperial clay	35.1	+.40	+.40	+.40	+.39	+.39	+.39
17	Keyport loam	13.2	+.16	+.14	+.11	+.10	+.09	+.07
17	do	26.3	+.38	+.35	+.31	+.29	+.26	+.24
20	Mahoning silt loam	13.2	+.36	+.34	+.32	+.31	+.30	+.28
23	Merced silt loam	8.8	−.06	−.06	−.07	−.07	−.07	−.08
23	do	87.7	+.38	+.37	+.35	+.34	+.34	+.32
28	Montezuma clay adobe	4.4	−.12	−.13	−.13	−.14	−.14	−.14
28	do	35.1	+.12	+.11	+.10	+.10	+.09	+.09
64	Salinas clay adobe	8.8	−.22	−.22	−.22		−.22	−.23
43	Tidal marsh	35.1	+.37	+.36	+.36	+.36	+.36	+.36
45	Unidentified alkali soil	8.8	−.01	−.01	−.02	−.02	−.02	−.03
45	do	35.1	+.12	+.12	+.11	+.10	+.10	+.08
			Cathode potentials[2]					
20	Mahoning silt loam	13.2	−0.82	−0.81	−0.79	−0.79	−0.77	−0.77
			Anode potentials[2]					
17	Keyport loam	26.3	−0.38	−0.35	−0.31	−0.29	−0.26	−0.24

[1] Numbers refer to test sites of National Bureau of Standards soil-corrosion investigation.
[2] Potentials measured with respect to saturated calomel electrode.

Since the period of interruption of the current is related to the resistance R_2 in the interrupter circuit, varying this resistance provides a convenient means for varying the period of interruption, and hence

for studying the rate of depolarization of the soil cells. In table 2 have been tabulated the measured voltages of soil cells for different periods of interruption corresponding to the value of resistance shown in the table. The soils selected for study exhibit a wide range of chemical and physical properties. It will be recalled from figure 2 that negative values indicate that the open-circuit voltage of the cell is greater than the voltage produced by polarization.

The rates of depolarization of the soil cells are seen to be subject to wide variation. In a few soils the maximum difference in voltage between the shortest and longest period of interruption was little more than 0.01 volt. In other soils this difference was 0.1 volt or more. It is of some interest to note from the measurements of separate electrode potentials that rapid depolarization may occur at the anode as well as the cathode.

IV. MEASUREMENT OF POTENTIALS BY MEANS OF ALTERNATING CURRENT WITH ELIMINATION OF *IR* DROP

An alternate method for measuring electrode potentials made use of both alternating and direct current. This method is based on the fact that if, for a given resistance, the peak value of *IR* drop with alternating current is equal to the *IR* drop with direct current, the two *IR* drops will be equal for any other resistance, as for example, the resistance of a cell whose voltage is to be measured. If the peak value of alternating current introduced in a circuit in which direct current is flowing is made equal to the direct current, it is evident that for an instant in each cycle the cell current and hence the *IR* drop in the cell will be zero. If a vacuum-tube voltmeter for measuring peak voltages or other suitable instrument is connected across the cell, electrode potentials at this instant can then be measured. In the present study, the electronic potentiometer described in the previous section was used for measuring potentials by this method. The circuit diagram is shown in figure 4.

The direct current in the cell circuit is adjusted to the desired values, as indicated by a direct-current milliammeter. With the thyratron in the measuring circuit (fig. 3) adjusted to its critical point, as indicated by the slow regular ticking in the loudspeaker, the measuring circuit is connected across resistor R_1 (fig. 4), P_3 being set at zero. As the grid of the thyratron is made more negative by the *IR* drop across the resistance, the ticking ceases. The alternating current is then adjusted until the critical point is restored. At this point the *IR* drop for the peak alternating and direct currents is the same, not only for the resistor but also for the cell regardless of its resistance. The measuring circuit is now connected across the cell and the critical point restored by changing the grid potential of the thyratron. The reading of the voltmeter at the critical point measures the potential difference between the anode and cathode of the cell or, if a reference electrode is used, the potential of each electrode is measured.

The test resistance in the circuit should have a value at least equal to the resistance of the cell. Otherwise, any error in adjustment with the voltmeter connected across the resistor would be increased when the voltmeter is connected across the cell. It is also essential that the voltage of the alternating current be constant over the interval during which the voltage is measured. The alternating current is adjusted

by a potentiometer in the primary circuit of the transformer so as not to change the resistance, and therefore the direct current, in the cell circuit. As with the interrupter method, the measuring circuit is so connected to R_1 (fig. 3) and the cell that the *IR* drop in the current circuit makes the grid of the thyratron more negative.

The frequency of the alternating current necessarily has an important bearing on the accuracy of the potential measurements, particularly if the rate of depolarization is rapid. As the direct current is alternately opposed and increased by the alternating current, the potential of the electrodes necessarily varies with the fluctuating current. Since the average value of the polarizing current is reached when the alternating current is zero, it follows that at that point in the cycle when the potential is measured, that is, when the *IR* drop is zero, the voltage of the cell is different from its average value, depending on the rate of depolarization of the cell and the frequency of the current. With 60-cycle current, which was the only frequency available with the required constant voltage, some depolarization occurred

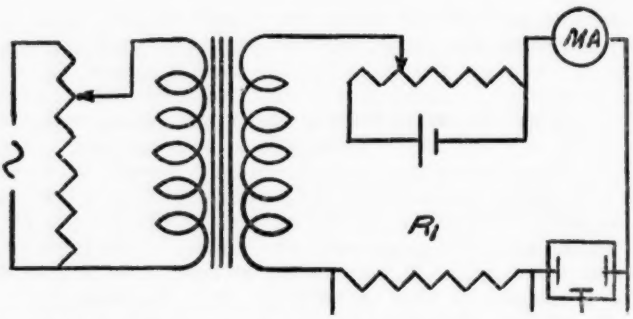


FIGURE 4.—*Circuit diagram of method employing alternating current.*

in the case of those cells which depolarized rapidly, as will be seen later. However, as the primary purpose of this method was to test the effect of cell resistance on the accuracy of the Hickling method, only cells which did not depolarize rapidly were used for comparison. For testing the accuracy of the Hickling method in cells which depolarized with extreme rapidity, the direct method, using continuous current, was employed. It is probable that the accuracy of the method could be improved by increasing the frequency of the alternating current.

V. MEASUREMENT OF POTENTIAL DIFFERENCE BETWEEN THE ANODE AND CATHODE

Measurements were made of the voltage between the anode and cathode in a group of soil-corrosion cells of low resistance. For each value of current the voltage across the cell was measured with a high-resistance voltmeter. The voltage measurements were corrected for *IR* drop, which was calculated from the current and the alternating-current resistance of the cell. Because of the tendency of the resistance of cells containing soils of high resistivity to vary with current, measurements were necessarily restricted to low-resistance cells. In the particular cells used, no change in cell resistance could be detected between the extremes of applied current. Corrections in resistance

measurements made for capacitance in the cells were negligible, as were corrections for the accuracy of the voltmeter and ammeter and the resistance of the voltmeter.

VI. COMPARISON OF POTENTIAL MEASUREMENTS BY DIFFERENT METHODS

Potential measurements made during interruption of current are necessarily subject to some uncertainty, even when the shortest time interval is utilized. In order to arrive at values for the instantaneous potentials of electrodes which depolarized with extreme rapidity, both Glasstone [4] and Hickling [3] found it necessary to plot potentials measured at various periods of interruption and to extrapolate to zero time. As such relations are empirical, it does not necessarily follow that the extrapolated values are always correct. For this reason it was considered especially important to compare the measurements made with the Hickling method with those obtained by an alternate method, preferably one which required the use of continuous current.

In table 3 are shown values for single electrode potentials and potential differences between the anode and cathode measured by the Hickling method. Potential differences measured by the direct method are also shown for comparison. It will be noted that the values measured by the two methods do not differ by more than 0.01 volt.

TABLE 3.—*Potential measurements made by the Hickling method and the direct method*

[Soil 113. Imperial clay. Cell resistance, 6.5 ohms]

Current density	Hickling method				Direct method (corrected) anode to cathode
	Anode	Cathode	Difference	Anode to cathode (measured)	
ma/dm	*v*	*v*	*v*	*v*	*v*
0	0.62	0.58	−0.04	−0.04	
1	.60	.58	−.03	−.02	−0.02
2.5	.60	.58	−.01	.00	.60
5	.58	.59	+.01	+.02	+.01
10	.56	.62	+.06	+.05	+.05
20	.54	.70	+.16	+.15	+.16
30	.53	.78	+.25	+.25	+.26
40	.52	.83	+.31	+.31	+.31

Before drawing final conclusions concerning the accuracy of the Hickling method as a general method for measuring electrode potentials in soils, it is obviously necessary that comparative measurements with other methods be made on soils which show a wide range of properties. The soils selected range in reaction between pH 3.1 and 9.4, in resistivity between 60 and 7,000 ohm-cm, and in texture from porous loams to an extremely heavy clay.

In table 4 are given values of the potential difference between the anode and cathode obtained by the three methods which have been described. Because of the inaccuracy of the direct method when applied to cells of high resistance, measurements in such cells were not made by this method.

It will be noted that the values given in the two columns for the Hickling method are not identical. These measurements were made at different times, between which the potentials of the electrodes had changed slightly.

TABLE 4.—*Measurements of potential differences between anode and cathode by different methods*

Soil		Cell resistance	Current density	Hickling method	Direct method	Hickling method	Alternating current method
No.	Type						
		Ohms	*ma/dm²*	*v*	*v*	*v*	*v*
103	Billings silt loam	13	8.8	−0.17	−0.18	−0.19	−0.19
			17.5	−.09	−.09	−.10	−.11
			26.3	−.03	−.04	−.03	−.05
			35.1	+.01	.00	+.02	−.02
45	Unidentified alkali soil	57	4.4	−.04	−.04	−.03	−.04
			8.8	−.01	−.02	.00	−.01
			17.5	+.04	+.03	+.04	+.04
			35.1	+.12	+.11	+.14	+.12
23	Merced silt loam	85	4.4	−.13	−.14	−.11	−.12
			8.8	−.09	−.09	−.06	−.07
			13.2	−.04	−.05	−.01	−.03
			26.3			+.10	+.08
			43.9			+.21	+.18
			78.9			+.36	+.33
28	Montezuma clay adobe	92	4.4	−.12	−.12	−.13	−.14
			8.8	−.06	−.07	−.07	−.08
			17.5	+.02	+.01	+.02	+.01
			35.1	+.12	+.11	+.13	+.10
41	Summit silt loam	105	4.4	−.06	−.07	−.07	−.09
			8.8	.00	−.01	+.01	−.01
			13.2	+.05	+.04	+.07	+.05
35	Ramona loam	407	.4			+.10	+.10
			.9			+.20	+.20
			1.8			+.52	+.51
26	Miami silt loam	435	4.4			+.20	+.19
			8.8			+.36	+.35
			17.5			+.67	+.65
4	Chester loam	1072	.4			+.21	+.20
			.9			+.50	+.50
			1.3			+.53	+.52

The average error between the Hickling method and the direct method is within 0.01 volt for every soil for which comparative data are given. While it cannot be stated that the true electrode potentials were measured by either the Hickling or the direct method, the consistently good agreement which was obtained indicates that the true values were at least closely approached.

The agreement between the Hickling method and the alternating-current method was generally good except in those cells in which depolarization was especially rapid. As would be expected, the error between the two methods becomes greater as higher current densities are applied. The values for the Merced silt loam illustrate these tendencies. It will be noted that the differences between the two methods in this soil gradually increase with increasing current density, reaching a maximum difference of 0.03 volt at the highest current density. By referring to table 2, it is seen that the polarization voltage in this cell at about the same current density drops 0.03 volt

when the resistance in the interrupter circuit is increased from 100 to 400 ohms.

The fact that there is disagreement between the Hickling method and the alternating-current method in certain soils was to be expected when low frequency current was used for the latter method. The significant fact is that the Hickling method is not subject to error from cell current and resistance within the range typical for high-resistance cells, as shown by good agreement between this method and the alternating-current method in high-resistance cells in which rapid depolarization was not a source of error. However, the data in table 1 indicate that errors are small over a much wider range of current and resistance, even when the rate of depolarization is rapid.

Although the modifications which have been introduced into the Hickling method were for the purpose of adapting it to measurements in soils, it would seem that the method as modified would be well adapted to high-resistance solutions, such as natural waters, particularly in connection with potential measurements of metals which naturally develop high-resistance films.

VII. REFERENCES

[1] I. A. Denison, J. Research NBS **17,** 363 (1936) RP918.
[2] I. A. Denison and R. B. Darnielle, Trans. Electrochem. Soc. **76,** 199 (1939).
[3] A. Hickling, Trans. Faraday Soc. **33,** 1540 (1937).
[4] S. Glasstone, J. Chem. Soc. **123,** 2926 (1923); **125,** 250 (1924).
[5] E. Newbery, Trans. Electrochem. Soc. **58,** 187 (1930).
[6] S. Evershed, J. Inst. Elec. Engrs. (London) **52,** 51 (1914).

WASHINGTON, June 17, 1940.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1337

Part of Journal of Research of the National Bureau of Standards, Volume 25, October 1940

EFFECTS OF DRYING CONDITIONS ON PROPERTIES OF TEXTILE YARNS

By James G. Wiegerink [1]

ABSTRACT

Yarns made from raw cotton, "purified" cotton, mercerized cotton, clothing wool, carpet wool, viscose rayon, cuprammonium rayon, cellulose acetate, and degummed silk were saturated with water and then exposed for periods of ½ to 6 hours in air having temperatures of 221°, 257°, and 302° F and absolute humidities of approximately 1, 55, and 95 percent, respectively. After conditioning the dried yarns for at least 24 hours in air of 65-percent relative humidity and 70° F, measurements were made of the breaking strengths, elongations at break, and moisture contents of the yarns; the fluidities of dispersions of the cellulosic fibers in cuprammonium solution, of the silk in aqueous zinc chloride, and of the acetate in aqueous acetone; and the relative affinities of the cellulosic fibers for the dye benzopurpurine *4B* and of the wools for acid dyes.

Heating the yarns for 6 hours at 221° F at each of the three humidities weakened all of them. The breaking strength and elongation at break of the viscose, cuprammonium, degummed silk, and cotton yarns decreased still more at higher temperatures. In comparison with heating at 1-percent absolute humidity, heating at 95-percent absolute humidity resulted in lower breaking strengths and elongations at break for all yarns except the raw cotton, higher fluidities, lower affinity of cellulosic fibers, and higher affinity of wool fibers for the dyes.

Heating for ½ hour at 302° F had little effect on the properties of the yarns except the viscose and cuprammonium rayon, which were adversely affected. The damage which occurred at a given temperature and humidity increased throughout the heating period.

CONTENTS

	Page
I. Introduction	435
II. Materials	436
III. Procedure	436
IV. Results and conclusions	438

I. INTRODUCTION

Although it is common knowledge that textile fibers are degraded at elevated temperatures, the combined effects of heat and moisture have received little study. Therefore, particular attention was given to this subject in the course of the studies of textile drying carried out by the United States Institute for Textile Research and the National Bureau of Standards.

The materials which are dried in the various branches of the textile industry, including laundries and dry-cleaning plants, and the procedures used are so various that no one set of materials and conditions can be considered representative of all of them. By limiting the work to yarns made from the common fibers freed from the natural nonfibrous materials which would be removed from them in the course of

[1] Research Associate at the National Bureau of Standards, representing the United States Institute for Textile Research. The establishment of this research associateship was made possible by funds contributed by 57 manufacturers.

manufacture, and to controlled and duplicable conditions of temperature, relative humidity, airflow, and thoroughness of exposure, it was possible to obtain data which may be considered basic to all types of textile drying. The results are given in this paper.

II. MATERIALS

The characteristics of the yarns and the purification treatments they received are given below. Where treatment with water is indicated, distilled water was used.

The raw cotton yarn (1/24)[2] was washed thoroughly in water. The "purified" cotton yarn was prepared from the raw cotton yarn by successive extractions with alcohol, ether, and 1-per cent NaOH solution, followed by rinsing in 5-percent acetic acid solution and then in water. The mercerized cotton yarn (2/25) was washed in a 5-percent NH_4OH solution, then rinsed in water. The clothing wool yarn (2/2.3) and the carpet wool yarn (3/1.2) were extracted with alcohol and ether, and rinsed in warm water. The viscose-rayon yarn (1/30; commercial designation 150 denier, 40 filament), the cuprammonium-rayon yarn (1/30; commercial designation 150 denier, 112 filament), and the cellulose-acetate yarn (1/30; commercial designation 150 denier, 46 filament) were washed in a warm 1-percent NH_4OH solution, then rinsed in warm water. The degummed silk yarn was prepared from a raw silk yarn (4/75) by degumming with an olive oil soap solution, followed by rinsing in warm water.

III. PROCEDURE

The equipment for this investigation is described in detail in a previous paper.[3] It provides means for controlling the temperature and humidity of air, for passing a stream of this air through a working chamber at a known rate, for supporting samples in this chamber so they are well exposed to the air stream, and for sampling the air in the working chamber and accurately determining its humidity by a gravimetric measurement of the moisture content. The temperature in the working chamber was maintained constant within $\pm 1°$ F and the humidity within ± 1 percent throughout each test. Three humidities at each temperature were studied. Hereafter, where a low, medium, and high humidity are referred to, absolute humidities of approximately 1, 55, and 95 percent, respectively, are meant. Relative humidities corresponding to these absolute humidities are also included for comparison.[4]

The samples for test were soaked overnight in distilled water. The following day the excess water was removed by squeezing the yarns until their weights were approximately 50 percent more than their "dry" weights (determined by heating other samples in an oven at 220° F for over 12 hours). The samples were then placed in the working chamber, which was maintained at the definite temperature

[2] The typp system for designating sizes of yarns is employed. The first number (1 in the case of the raw cotton yarn) indicates the number of units of which the yarn is composed, that is, the ply. The second number (24 in the case of the raw cotton yarn) indicates the number of thousands of yards of the finished yarn in 1 pound.

[3] J. G. Wiegerink, *Equipment for conditioning materials at constant humidities and at elevated temperature*, J. Research NBS **24**, 639 (1940) RP1303.

[4] The term "relative humidity" as used in this report is the ratio of the actual pressure of water vapor to the maximum possible pressure of water vapor in the atmosphere at the same temperature, expressed as a percentage. The term "absolute humidity" as used in this report is the actual percentage by volume of water vapor in the system.

and humidity of the test. The samples were kept in the chamber for different intervals of time ranging from ½ to 6 hours. All samples came to practically constant weight before removal from the working chamber and consequently contained an amount of moisture consistent with the relative humidity and temperature of the test. These equilibrium values at the various relative humidities and temperatures are reported in a previous paper.[5] It should be noted that all samples were placed in the working chamber wet, and that during evaporation of the moisture the textile was at a lower temperature than that indicated by the dry-bulb temperature in the working chamber. Thus, where a ½- to 1-hour heat treatment at a certain dry-bulb temperature is indicated, the samples, although dried to equilibrium before being taken from the working chamber, may have been at the dry-bulb temperature for less than 15 minutes during the ½-hour exposure and less than ½ hour during the 1-hour exposure.

The samples were removed from the working chamber and conditioned for at least 24 hours in an atmosphere of 65-percent relative humidity at 70° F. They were tested in this atmosphere, using a pendulum single-strand tester. The distance between the jaws of the testing machine at the start of each test was 10 inches, and the speed of separation of the jaws was 12 inches per minute. The breaking strength and elongation at break were observed.

The fluidities of dispersions in cuprammonium solution of the dried raw cotton, the purified cotton, and the viscose rayon were measured with the method described by Mease.[6] These dispersions contained 0.5 g of the cotton, or 2.5 g of the viscose rayon, dry basis (calculated from the moisture content determined on a duplicate sample) for 100 ml of dispersion. Measurements were made of the fluidity of the dried degummed silk in aqueous zinc chloride solution, density 1.67 at 70° F, 2.5 g of the silk, dry basis, being used for 100 ml of solvent. The weighed amount of the silk, cut into small pieces, was introduced into a small flask, and the required volume of zinc chloride solution added. The flask was then stoppered and placed in an oven at 113° F for 3 hours, with occasional swirling of the flask to ensure mixing of the contents. The solution was then cooled to 70° F, transferred to a viscosimeter, and the viscosity measured at 70° F.[7]

The fluidity of the dried cellulose acetate was measured in aqueous acetone, density 0.81 at 70° F, 2.5 g of the acetate, dry basis, being used for 100 ml of solvent. The weighed amount of acetate was dissolved in the required volume of acetone, and kept at 70° F overnight. In the morning the solution was transferred to a viscosimeter and the viscosity at 70° F measured. The fluidities of the original samples, not dried, were measured for comparison with the dried samples.

The moisture contents of the heat-treated yarns, after conditioning them for 24 hours or more in an atmosphere of 65-percent relative humidity and 70° F, were determined in the usual manner.

The heat-treated cellulosic yarns, namely viscose rayon, cupram-

[5] J. G. Wiegerink, *The moisture relations of textile fibers at elevated temperatures*, J. Research NBS **24**, 645 (1940) RP1304.

[6] R. T. Mease, *Measurement of the apparent fluidity of dispersions of cellulose in cuprammonium solution*, J. Research NBS **22**, 3 (1939) RP1179.

[7] A. S. Tweedie, *A study of the viscosity method for the determination of damage in silk*, Can. J. Research **16***B*, 134-150 (1938).

monium rayon, purified cotton, and mercerized cotton, were dyed with a solution containing 0.5 percent of benzopurpurine *4B* and 10 percent of NaCl, based on the weight of the yarn. The heat-treated clothing and carpet wools were dyed with a solution containing 0.3 percent of alizarine astrole *B*, 0.1 percent of fast light yellow *2G*, 0.25 percent of neolan red *3B*, 20 percent of Glauber's salt, and 5 percent of sodium bisulfate. The dyed yarns were wound on dark cardboard and their spectral reflectances relative to magnesium oxide were determined at a wavelength of 501 millimicrons. This wavelength was chosen after a study of the complete reflectance curves (400 to 740 λ) for typical samples.

The cystine contents of the heat-treated samples of clothing wool were determined by the Sullivan method.[8]

IV. RESULTS AND CONCLUSIONS

Tables 1 to 9 give the breaking strengths, elongations at break, and "quality indices" of the yarns, after being heated at different humidities for various periods of time and then exposed to the standard conditions of 65-percent relative humidity and 70° F for at least 24 hours. Each value is the average of 25 tests. The "quality index" is the percentage of the original breaking strength after drying, multiplied by the percentage of the original elongation after drying. It appears to be useful in analyzing the results.

TABLE 1.—*Viscose rayon yarn*

Temperature (°F)	Relative humidity[1]	Absolute humidity[1]	Time of exposure	Breaking strength (as % of original)	Elongation at break (as % of original)	Quality index
	%	%	*hr*			
221	1	1	1	95	97	92
			1½	94	97	91
			6	90	89	80
221	48	57	1½	99	93	92
			3	100	91	91
			6	97	84	81
221	79	94	1½	96	97	93
			4	97	91	88
			6	90	83	75
257	0.5	1	½	92	91	84
			1½	85	79	67
			6	72	67	48
257	24	55	¾	96	86	82
			1¾	85	72	61
			6	72	56	40
257	42	96	½	99	93	92
			1½	90	82	74
			6	68	57	38
302	0.2	0.5	½	73	61	45
			1½	67	58	39
			6	50	42	21
302	12	56	½	69	54	37
			1½	57	38	22
			6	45	23	10
302	20	96	½	83	70	58
			1½	60	50	30
			6	43	27	11

[1] See footnote 4 of text.

[8] M. X. Sullivan, Public Health Reports 86 (1930).

TABLE 2.—*Cuprammonium rayon yarn*

Temperature (°F)	Relative humidity	Absolute humidity	Time of exposure	Breaking strength (as % of original)	Elongation at break (as % of original)	Quality index
	%	%	*hr*			
221	1	1	1	100	94	94
			2	100	94	94
			6	100	94	94
221	48	57	1½	97	85	82
			3	94	76	71
			6	86	67	58
221	79	94	2	98	79	77
			4	96	61	59
			6	92	58	53
257	0.5	1	½	100	97	97
			1½	96	91	87
			6	96	85	82
257	24	55	¾	97	85	82
			1¾	89	70	62
			6	77	55	42
257	42	96	1	98	79	77
			2	87	58	50
			6	76	45	34
302	0.2	0.5	½	94	79	74
			1½	93	73	68
			6	76	55	42
302	12	56	½	89	73	65
			1½	79	60	47
			6	65	36	23
302	20	96	½	86	67	58
			1½	71	42	30
			6	56	24	13

TABLE 3.—*Clothing wool yarn*

Temperature (° F)	Relative humidity	Absolute humidity	Time of exposure	Breaking strength (as % of original)	Elongation at break (as % of original)	Quality index	Cystine content (original =11.5)
	%	%	*hr*				%
221	1	1	1	102	100	102	----
			2	99	100	99	----
			6	95	93	88	11.3
221	48	57	1½	95	97	92	----
			3	91	91	83	----
			6	91	91	83	11.2
221	79	94	2	100	100	100	----
			4	97	89	86	----
			6	95	86	82	9.6
257	0.5	1	½	100	100	100	----
			1½	91	93	85	----
			6	91	93	85	11.3
257	24	55	¾	105	98	103	----
			1¾	97	97	94	----
			6	95	93	88	11.1
257	42	96	1	100	98	98	----
			2	98	93	91	----
			6	94	89	84	9.5
302	0.2	0.5	½	99	100	99	----
			1½	92	97	89	----
			6	91	93	85	10.3
302	12	56	½	107	93	100	----
			1½	93	91	85	----
			6	91	91	83	10.3
302	20	96	½	100	97	97	----
			1½	96	93	89	----
			6	90	85	77	8.8

TABLE 4.—*Carpet wool yarn*

Temperature (°F)	Relative humidity	Absolute humidity	Time of exposure	Breaking strength (as % of original)	Elongation at break (as % of original)	Quality index
	%	%	*hr*			
221	1	1	1	92	100	92
			2	87	95	83
			6	87	85	74
221	48	57	1½	89	90	80
			3	87	85	74
			6	87	85	74
221	79	94	2	78	90	70
			4	78	85	66
			6	78	77	60
257	0.5	1	½	95	100	95
			1½	91	90	82
			6	89	85	76
257	24	55	¾	84	85	71
			1¾	81	80	65
			6	86	85	73
257	42	96	1	81	90	73
			2	84	80	67
			6	82	80	66
302	0.2	0.5	½	94	100	94
			1½	89	90	80
			6	86	85	73
302	12	56	½	87	90	78
			1½	84	90	76
			6	81	85	69
302	20	96	½	89	85	76
			1½	83	75	62
			6	81	75	61

TABLE 5.—*"Purified" cotton yarn*

Temperature (°F)	Relative humidity	Absolute humidity	Time of exposure	Breaking strength (as % of original)	Elongation at break (as % of original)	Quality index
	%	%	*hr*			
221	1	1	1½	99	97	96
			6	95	97	92
221	48	57	1½	100	98	98
			6	93	91	85
221	79	94	1½	91	94	86
			6	87	89	77
257	0.5	1	1½	100	102	102
			6	92	93	86
257	24	55	1½	93	89	83
			6	85	87	74
257	42	96	1½	87	90	78
			6	78	81	63
302	0.2	0.5	½	98	95	93
			1½	94	93	87
			6	84	82	69
302	12	56	½	92	90	83
			1½	79	80	63
			6	68	67	46
302	20	96	½	96	100	96
			1½	82	85	70
			6	58	69	40

TABLE 6.—*Raw cotton yarn*

Temperature (°F)	Relative humidity	Absolute humidity	Time of exposure	Breaking strength (as % of original)	Elongation at break (as % of original)	Quality index
	%	%	*hr*			
221	1	1	1½	95	94	89
			6	94	93	87
221	48	57	1½	89	100	89
			6	92	95	87
221	79	94	1½	93	95	88
			6	95	92	87
257	0.5	1	1½	89	90	80
			6	88	90	79
257	24	55	1½	98	95	93
			6	93	90	84
257	42	96	1½	90	90	81
			6	92	88	81
302	0.2	0.5	½	96	90	86
			1½	94	90	85
			6	89	84	75
302	12	56	½	94	90	85
			1½	91	85	77
			6	89	80	71
302	20	96	½	85	90	77
			1½	89	86	77
			6	84	83	70

TABLE 7.—*Mercerized cotton yarn*

Temperature (°F)	Relative humidity	Absolute humidity	Time of exposure	Breaking strength (as % of original)	Elongation at break (as % of original)	Quality index
	%	%	*hr*			
221	1	1	1	91	90	82
			2	92	95	87
			6	108	105	113
221	48	57	1½	92	95	87
			3	98	96	94
			6	105	97	102
221	79	94	2	92	94	86
			4	97	95	92
			6	94	93	87
257	0.5	1	½	96	96	92
			1½	92	94	86
			6	99	96	95
257	24	55	¾	97	96	93
			1¾	88	90	79
			6	100	98	98
257	42	96	1	87	92	80
			2	92	90	83
			6	88	89	78
302	0.2	0.5	½	94	93	87
			1½	90	91	82
			6	92	95	87
302	12	56	½	97	95	92
			1½	87	89	77
			6	91	93	85
302	20	96	½	93	90	84
			1½	88	89	78
			6	89	89	79

259104—40——4

TABLE 8.—*Degummed silk yarn*

Temperature (°F)	Relative humidity	Absolute humidity	Time of exposure	Breaking strength (as % of original)	Elongation at break (as % of original)	Quality index
	%	%	*hr*			
221	1	1	1	96	100	96
			2	96	100	96
			6	96	100	96
221	48	57	1½	100	92	92
			3	98	88	86
			6	93	90	84
221	79	94	2	99	92	91
			4	99	92	91
			6	99	90	89
257	0.5	1	½	99	99	98
			1½	96	93	89
			6	93	88	82
257	24	55	¾	94	85	80
			1¾	91	84	76
			6	89	81	72
257	42	96	1	100	86	86
			2	99	84	83
			6	89	78	69
302	0.2	0.5	½	90	89	80
			1½	88	84	74
			6	74	75	56
302	12	56	½	93	98	91
			1½	92	85	78
			6	76	74	56
302	20	96	½	96	91	87
			1½	95	89	85
			6	76	74	56

TABLE 9.—*Acetate yarn*

Temperature (°F)	Relative humidity	Absolute humidity	Time of exposure	Breaking strength (as % of original)	Elongation at break (as % of original)	Quality index
	%	%	*hr*			
221	1	1	1	100	98	98
			2	94	95	89
			6	94	95	89
221	48	57	1½	98	90	88
			3	98	93	91
			6	98	93	91
221	79	94	2	82	84	69
			4	83	85	70
			6	82	84	69
257	0.5	1	½	99	95	94
			1½	96	91	87
			6	95	95	90
257	24	55	¾	99	95	94
			1¾	98	95	93
			6	93	92	86
257	42	96	1	100	87	87
			2	99	84	83
			6	100	86	86
302	0.2	0.5	½	98	95	93
			1½	100	95	95
			6	100	92	92
302	12	56	½	100	91	91
			1½	98	91	89
			6	96	88	84
302	20	96	½	103	87	90
			1½	102	85	87
			6	96	84	81

The relationships between temperature and humidity of drying, on the one hand, and quality index, fluidity, moisture content, and affinity for dyes of the dried conditioned fibers, on the other hand, are shown in figures 1 to 4, respectively. The data are for the 6-hour treatment, the maximum time of exposure used in the experiments. The solid lines in the figures indicate the averages of the values for the different humidities at constant temperature. These lines show in a general way the effects of heat, while the departures of the points show the effects of humidity. It should be emphasized that the results and conclusions based on them apply only to the samples examined. Further work is necessary to determine what variation is to be expected in different lots of the same fiber, or when the fibers contain oils, sizing materials, and dyes.

Figure 1 shows that the quality indices of all of the yarns were adversely affected by the temperatures at which the yarns were heated. All were decreased by heating for 6 hours at 221° F, and the lowering of the quality indices for the viscose and cuprammonium rayons, the degummed silk, and the cotton yarns was greater as the temperature was increased. Heating in air of an absolute humidity of approximately 95 percent tended to give lower quality indices for all of the yarns, except the raw cotton, than heating in air of an absolute humidity of approximately 1 percent. The greatest effect of humidity was obtained with the cuprammonium rayon, whose behavior was in marked contrast to that of the viscose rayon in this respect. Indeed, the effect of the humidity of the air on the quality index of cuprammonium rayon was as great as that of the change in temperature from 221° to 302° F.

The effects of heat on the clothing and carpet wool yarns were less than the effects of humidity as measured by the quality index, the average line being nearly horizontal. This is particularly true of the carpet wool yarn, which shows the greatest degradation at the high humidity. The results also indicate that the carpet wool is less resistant to heat and humidity than the corresponding clothing wool yarn.

Figure 1 indicates that heat had a greater effect on the quality indices of the purified and the raw cotton yarns than on the wool yarns. The purified cotton yarn was less resistant to heat treatment than the raw cotton yarn. The high humidity had a more degrading effect at constant temperature on the purified cotton yarn than the low humidity, but the raw cotton yarn was scarcely affected. This difference in behavior between the raw and the purified cotton yarns may be attributed to a protective action of the natural waxes in the raw cotton, which are removed by the caustic purification.

It appears from the results for the mercerized cotton and the acetate yarns that the effect of humidity, particularly the high humidity, which had the greatest degrading effect, was relatively more important than the effect of heat. In fact, the high humidity at 221° F gave the lowest quality index for the acetate yarn.

This low quality index for the acetate yarn dried at 221° F at the high humidity may be explained by the data given in table 9. The breaking strength of the acetate yarn was found to decrease only when the yarn was heated at 221° F at the high humidity. At any of the other conditions studied there was no significant decrease in the breaking strength. On the other hand, there were appreciable

variations in the elongation, which was lower at a high humidity at each temperature than at a low humidity. The yarns dried at the high humidity were more brittle than the yarns dried at the low

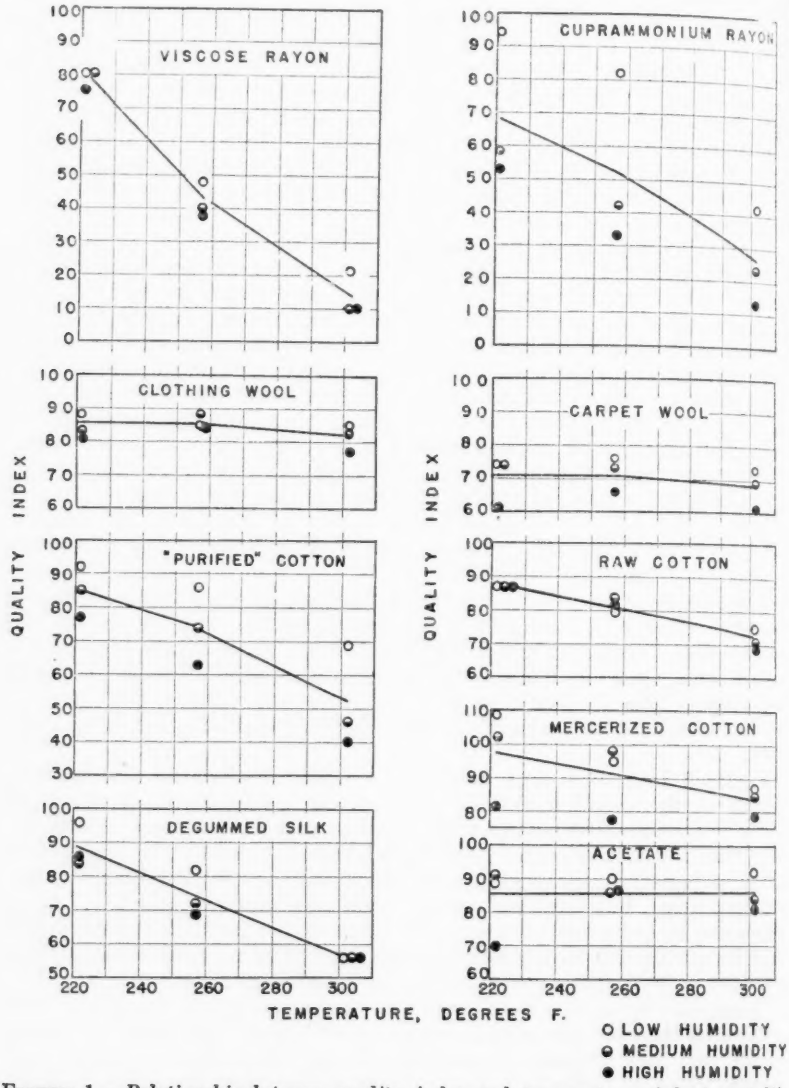


FIGURE 1.—*Relationship between quality index and temperature of drying at different humidities for 6-hour time of exposure.*

humidity, even after conditioning them. The fact that there was a decrease in breaking strength of the yarns heated at 221° F at the high humidity may indicate that this particular condition aids hydrolysis. The water in the acetate yarn before drying would be evaporated more slowly at 221° F at the high humidity than at any

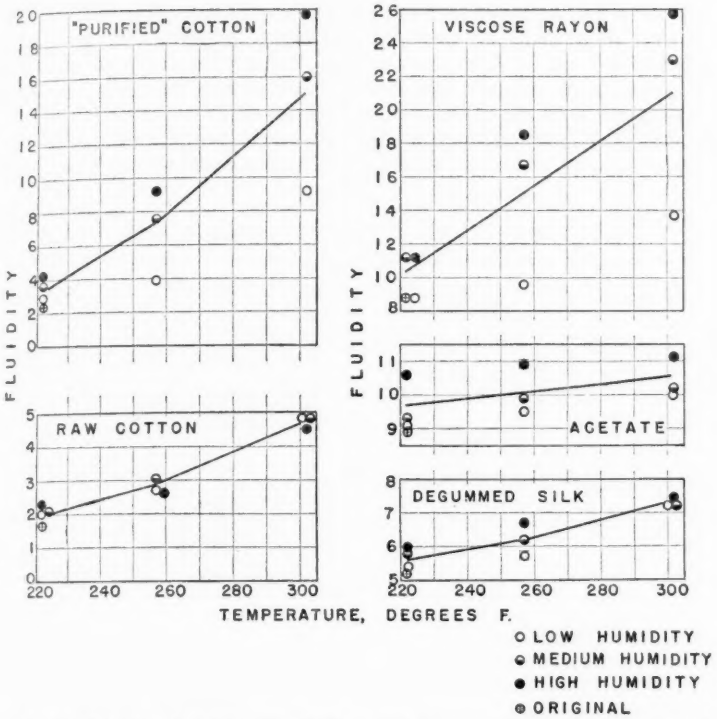


FIGURE 2.—*Relationship between fluidity and temperature of drying at different humidities for 6-hour time of exposure.*

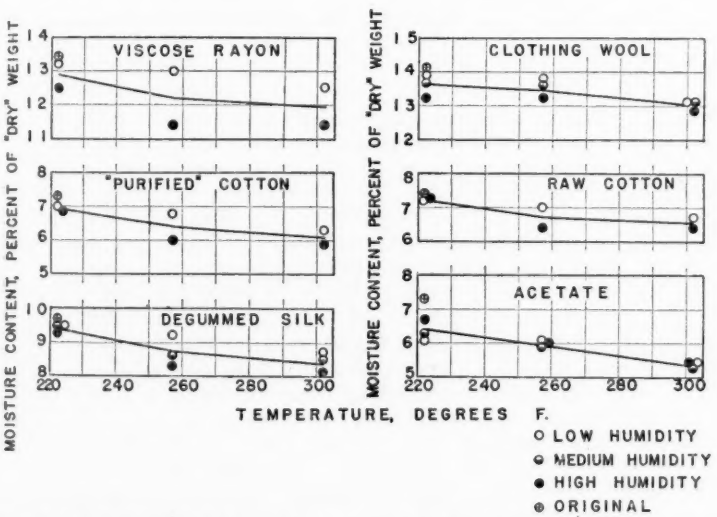


FIGURE 3.—*Relationship between moisture content on conditioning and temperature of drying at different humidities for 6-hour time of exposure.*

of the other conditions studied. It appears that carpet wool, which lends itself to hydrolysis, also showed a similar effect at this particular condition. It should be mentioned that the acetate yarns were under no tension during the drying treatments, so that this factor does not enter into the above considerations.

The effect of heat on the quality index of the degummed silk (fig. 1) was approximately of the same order as the effect on the purified

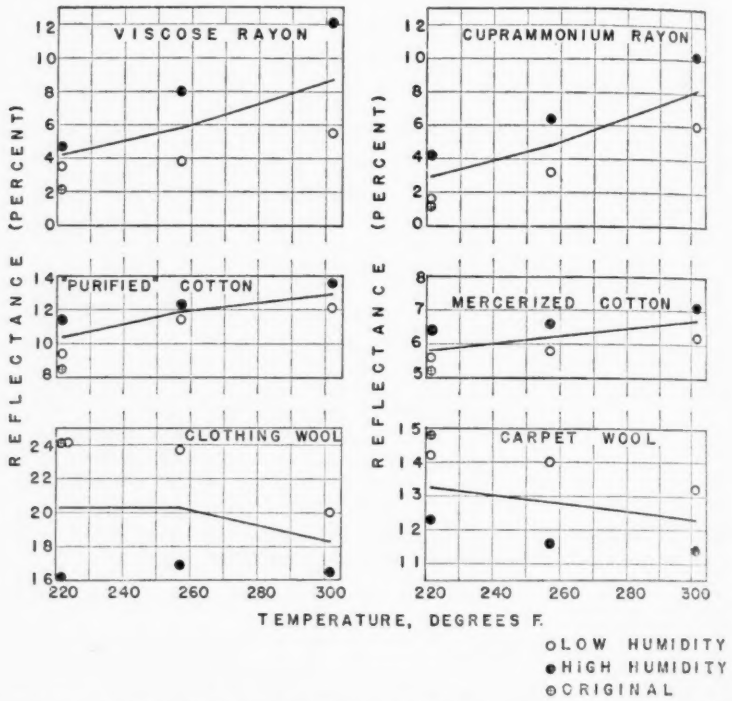


FIGURE 4.—*Relationship between reflectance and temperature of drying at different humidities for 6-hour time of exposure.*

cotton yarn. However, the effect of humidity at 302° F was somewhat different. The high humidity at 221° and 257° F had greater effect than the low humidity at these temperatures. No differences at 302° F in respect to humidity are indicated.

Figure 2 shows the relationships between temperature and humidity of drying, and fluidity for some of the yarns. The fluidities of the purified cotton and the viscose rayon in cuprammonium solution, of the degummed silk in aqueous zinc chloride, and of the acetate in aqueous acetone were increased by heating for 6 hours at 221° F, and these increases in fluidity were greater as the temperature was increased. The fluidities were higher after treatment at the high humidity than at the low humidity. This increase in fluidity indicates greater degradation and corresponds well with the quality indices of the dried fibers mentioned above. The fluidities of the dried raw cotton in cuprammonium solution, however, did not change with

change in humidity at constant temperature, an effect which was also found to be true for the quality indices.

Although the viscose rayon gave lower values of quality index for the high humidity at a given temperature, the differences were small. However, figure 2 indicates that the effect of humidity is important. The fluidities are much higher at the high humidity than at the low humidity, which indicates that at the temperatures studied the high humidity has a greater degrading effect than a low humidity.

Figure 3 shows the effects of heat and humidity on the moisture contents of the various textile materials when conditioned in an atmosphere of 65-percent relative humidity and 70° F. These values are given for the 6-hour treatment.

Each of the dried yarns failed to regain the amount of moisture it held originally. Yarns heated at the high humidity had a lower moisture content on conditioning than those heated at the low humidity, with the exception of the acetate yarn. The moisture contents of the acetate yarns on conditioning show little effect with respect to humidity, but the effect of heat is important. For example, yarns heated at 302° F for 6 hours had a moisture content of only 5.3 percent on conditioning at 65-percent relative humidity, 70° F, as compared with the 7.3 percent moisture content of the original sample for the same conditions.

Figure 4 shows the effects of the 6-hour treatments on the affinities of the various textile materials for dyes, as measured by changes in their spectral reflectances relative to MgO. An examination of figure 4 shows that the affinity of the dried cellulosic fibers for the dye benzopurpurine *4B* decreased, as indicated by the higher reflectance values. Also, the fibers heated at the high humidity for a given temperature adsorbed less of this dye than when heated at the low humidity. This is in agreement with the physical and chemical data given above.

The wool yarns, on the other hand, when degraded by heat and humidity treatments adsorbed more of the acid dyes. The wool yarns heated at the high humidity at a given temperature adsorbed more of the acid dyes than when heated at the low humidity, as indicated by the lower reflectance values. In fact, there is little difference in the reflectance at a low humidity for any of the temperatures investigated, but a high humidity even at the lowest temperature investigated, 221° F, gave low reflectance compared with the original. This difference in affinity of the dried clothing wool yarn for dyes corresponds to the difference in the cystine content (see table 3).

Figure 5 shows the relationship between breaking strength and fluidity of the dried and conditioned textile materials. The curves for the viscose rayon, the purified cotton, and the degummed silk indicate linear relations between fluidity and breaking strength, provided the humidity is taken into consideration. Little relationship was found between breaking strength and fluidity for the raw cotton. The changes in breaking strength and fluidity are small compared with those of the viscose-rayon and the purified-cotton yarns. The sharp break upward in the curve for the raw cotton yarn does indicate that the fluidity is more sensitive to changes in the fiber than the breaking strength of the yarn.

The acetate yarn is peculiar in that no relationship was found between breaking strength and fluidity. However, elongation plotted

against the corresponding fluidity gave an approximate linear relationship. This indicates that breaking strength is the least sensitive of the criteria used for judging degradation in the acetate yarn.

Figure 6 shows a definite relationship between the reflectance and the chemical and physical properties. The reflectances of the purified cotton and the viscose-rayon yarns change more rapidly than the fluidities in the first stages of apparent degradation. This may indi-

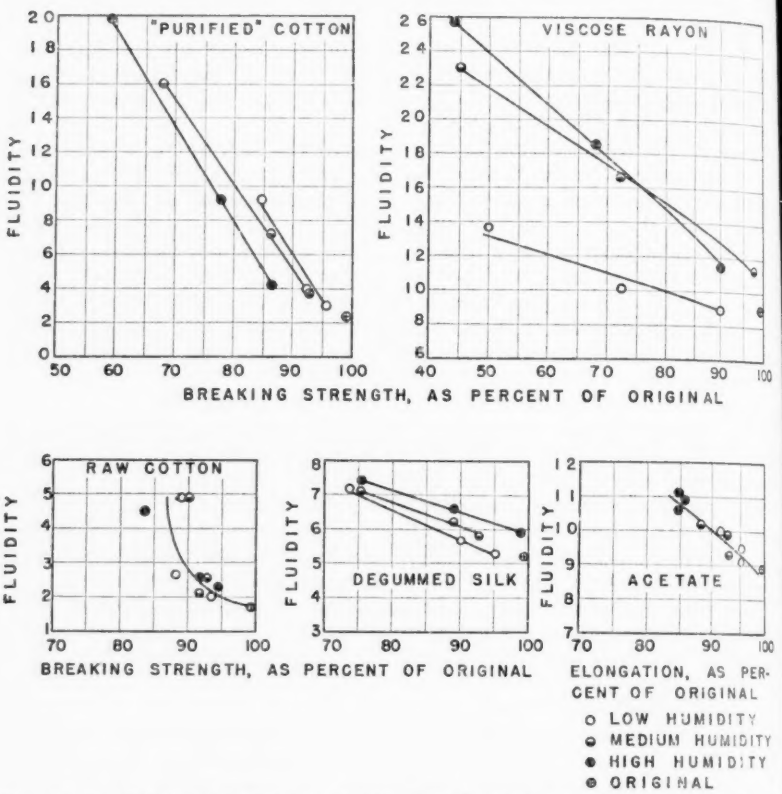


FIGURE 5.—*Relationship between fluidity and breaking strength as a function of humidity.*

cate merely that the dye test measures surface changes in the yarns, and that the fluidity measures mainly chemical changes.

The time of heating the yarns is also important. The conclusions mentioned above were drawn on the basis of the data for the 6-hour treatment. The tables give the results for short intervals of time as well as for the 6-hour period. An examination of tables 1 to 9 shows that for the shorter periods studied, ½, ¾, and 1 hour, most of the materials underwent very little decrease in breaking strength. A slightly greater effect on elongation at break is indicated. Several exceptions, however, are noted. There was some lowering in breaking strength and elongation at break of the carpet wool and acetate yarns when heated for a 2-hour period at 221° F at the high humidity. The viscose- and cuprammonium-rayon yarns, which were the least

resistant to heat of all the materials studied, showed a decrease in breaking strength and elongation if heated for only ½ hour at 302° F. The purified cotton yarn showed a small decrease in quality index on heating for ½ hour at 302° F.

There was an increase in fluidity of the viscose-rayon yarn after heating it for a short period at 257° F at the high humidity, and for

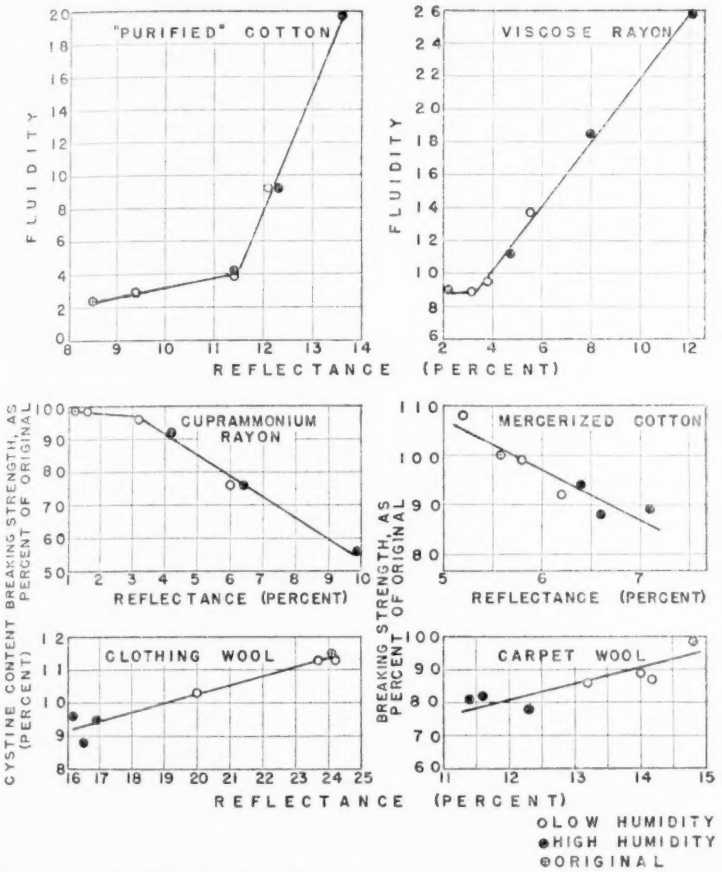


FIGURE 6.—*Relationship between reflectance and the physical and chemical data as a function of humidity.*

a short period at 302° F at all three humidities. The fluidity of the purified cotton yarn was approximately 4.0 rhes after ½-hour treatment at 302° F at all humidities, 9.1 rhes after 1½ hour at 302° F at the high humidity, as compared with the original sample with a fluidity of 2.4 rhes.

There was an increase in reflectance of dyeings of the viscose rayon, cuprammonium rayon, and purified cotton heated for only short periods of time, indicating a decrease in affinity for the dye. For example, dyeings were prepared after heating the yarns at 302° F for 1½ hours at the low humidity and at the high humidity. The

reflectances of the untreated yarns, yarns heated at the low humidity, and yarns heated at the high humidity, respectively, were: viscose rayon, 2.1, 4.4, and 5.7 percent; cuprammonium rayon, 1.2, 1.7, and 4.3 percent; purified cotton, 8.5, 10.8, and 10.7 percent.

The author expresses his thanks to A. C. Walker, chairman, and Frederic Bonnet, member, Administration Committee for Drying Research, United States Institute for Textile Research, and to W. D. Appel, of the National Bureau of Standards, for suggesting the investigation and for valuable advice throughout the course of the work.

The author thanks R. K. Worner for undertaking the fluidity measurements of the cellulosic fibers and H. Bogaty for assistance in the yarn testing.

WASHINGTON, July 2, 1940.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1338

Part of Journal of Research of the National Bureau of Standards, Volume 25, October 1940

REACTION OF SILK FIBROIN WITH DIAZOMETHANE

By Henry A. Rutherford, Wilbur I. Patterson, and Milton Harris[1]

ABSTRACT

The treatment of silk with an ethereal solution of diazomethane resulted in a rapid decrease in tyrosine content, with no appreciable decrease in tensile strength of the fibers. The results indicate that the hydroxyl groups of tyrosine in the untreated fibers are free. The total methoxyl content after treatment of the fiber for 25 hours or longer was greater than could be accounted for by assuming that only phenolic hydroxyl groups had reacted. The "extra" methoxyl was not on either the primary amino groups or on the hydroxyl groups of the amino acid serine, but appears to have resulted from the reaction of diazomethane with groups, tentatively assumed to be carboyxl, to form the methyl esters.

CONTENTS

	Page
I. Introduction	451
II. Experimental procedure	452
1. Materials and methods	452
2. Preparation of diazomethane	453
3. Methylation of fibroin	453
III. Results and discussion	454
1. Reaction of silk with diazomethane	454
2. Reaction of methylated silk with nitrous acid	457
IV. References	458

I. INTRODUCTION

Many of the chemical and physical properties of a protein are intimately related to the number and arrangement of its functional or reactive groups, most of which are contributed by the dibasic and diacidic amino acids. Silk fibroin is composed largely of the amino acids, glycine, alanine, and tyrosine, and of these only the last one would be expected to contribute a reactive group, namely, a phenolic hydroxyl group. This group thus becomes of special interest.

As the result of observations in this laboratory, it appeared that the hydroxyl groups of tyrosine might not be free in the untreated fiber. For example, it was found that when fibroin was treated at pH 8 with Folin's phosphomolybdate phenol reagent [1],[2] only a pale blue color, indicative of phenolic hydroxyl groups, was produced, but as the pH was increased, the solution became increasingly colored. Pretreatment of the silk with alkali also increased the depth of color obtained with this reagent. Similar results were obtained with other proteins (pepsin and wool), and it appeared that not all of the phenolic hydroxyl groups of these proteins were free. Further evidence favoring this view was obtained by Fruton and Lavin [2], who observed that the characteristic absorption bands of tyrosine were not found in

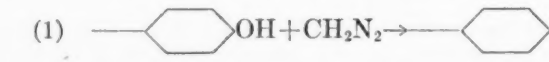
[1] Research Associates of the National Bureau of Standards, representing the Textile Foundation, Inc.
[2] Figures in brackets indicate the literature references at the end of this paper.

untreated papain, although, on acid hydrolysis, appreciable amounts of the amino acid were liberated.

The state of this hydroxyl group in the silk fiber becomes of considerable importance, since it would be expected to influence such properties of the fiber as tensile strength, extensibility, and absorption of moisture, acids, alkalies, or dyes. Unfortunately, the experiments indicating that the hydroxyl groups are not free must be considered inconclusive and open to some criticism, since they involve the use of treatments which are known to have a degradative effect on the protein. It appeared that a better approach to the problem might be made by attempting to cause the hydroxyl group to react with suitable mild chemical reagents under conditions which would minimize the possibility of degradation of the fibers.

Of the available reagents, the acid chlorides or anhydrides, ketene, and diazomethane, appear to be most suitable for inactivating the hydroxyl groups of tyrosine. The acid chlorides and anhydrides were used for this purpose by Abderhalden and Brockmann [3, 4], but they were found to produce appreciable deterioration of the fibers. Ketene was used by Kise and Carr [5, 6] with far more satisfactory results, although on prolonged treatment with this reagent the fiber was colored tan and some degradation occurred. The product of the reaction of ketene with the hydroxyl group of tyrosine is an ester, which is readily hydrolyzed in either alkaline or acid solutions. For this reason, it is not possible, by the usual tyrosine analyses, to estimate quantitatively the extent to which the ketene has reacted with the hydroxyl groups. Further, the acetyl value of the treated fiber is also inadequate for this purpose, since it is known that the ketene reacts with groups other than the phenolic hydroxyl group.

Diazomethane offers several advantages over the above-mentioned reagents. It can be used in neutral aqueous or organic solutions, and it reacts with a phenolic hydroxyl group to form an ether as follows:



The product of the reaction is stable during the alkaline hydrolysis used in tyrosine determinations, which makes possible the quantitative estimation of the extent to which the tyrosine has reacted. The reagent was used by Herzig and Landsteiner [7], and by Abderhalden and Brockmann [3], on several proteins, including silk, but the extent of the reaction with tyrosine was not determined. The methoxyl contents of the treated fibers, however, were found to be greater than would be expected if only the phenolic hydroxyl groups were reacting.

II. EXPERIMENTAL PROCEDURE

1. MATERIALS AND METHODS

Silk fibroin in the form of a plain-woven cloth was used in this work. Before treatment with diazomethane, it was extracted for 8 hours each with alcohol and with ether, and finally washed thoroughly with cold distilled water.

Total nitrogen was determined by the micro-Kjeldahl method; tyrosine by Lugg's method [8] after an alkaline hydrolysis; amino

nitrogen by the method of Rutherford, Harris, and Smith [9]; methoxyl content by the procedure described by Vieböck and Brecher [10]; and methyl alcohol by Beyer's method [11].

2. PREPARATION OF DIAZOMETHANE

The ethereal solution of diazomethane was prepared according to the method described by Adamson and Kenner [12]. The apparatus is shown in figure 1. The temperature of the reaction flask, *B*, was maintained at 75° to 80° C in a water bath, and that of the receiver, *A*, at −10° to −15° in a brine tank. Before the distillation of the diazomethane was started, about 100 ml of ether was added to flask

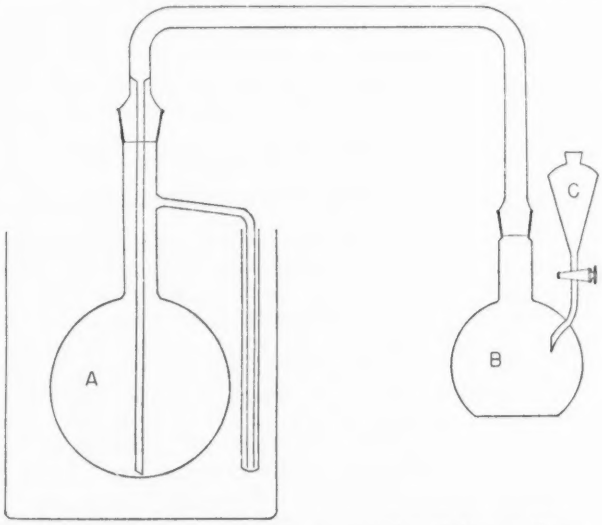


FIGURE 1.—*Apparatus for the preparation of diazomethane.*

A, and 10 ml to the trap at the side arm of *A*. 0.05-mole of the nitroso derivative of the methylamine addition product of mesityl oxide in 40 ml of ether and 6 ml of isopropanol was added dropwise from funnel *C* to 30 ml of 1-percent sodium isopropoxide in flask *B*, the rate of addition being slightly greater than that of distillation. When the addition was complete, 15 ml more of 1-percent sodium isopropoxide was added to *B*, followed by another 0.05-mole portion of the nitroso ketone, as before. Finally, ether was added to flask *B* until all the diazomethane was distilled into *A*. By this procedure about 1 g of diazomethane in 250 to 300 ml of ether was obtained. The actual amount was readily determined by the addition of an aliquot of the ether solution to a weighed quantity of benzoic acid, and subsequent titration of the excess acid with 0.1 *N* potassium hydroxide in alcohol [15].

3. METHYLATION OF FIBROIN

Preliminary experiments showed that the rate of methylation of the tyrosine hydroxyl groups of the silk was increased by the presence of a little moisture, by increased concentrations of diazomethane, or

by treating the fibers at low temperatures (−10° C or below). On the basis of these experiments, the following procedure was used. The sample was first wet thoroughly with 75-percent alcohol and then squeezed as dry as possible. This wetting served to introduce an appreciable quantity of water into the fiber, and when the sample was treated by this procedure, the subsequent separation of a water layer in the ether solution was avoided. The silk was then placed in flask *A* containing the diazomethane, and the reaction allowed to proceed at −10° to −15° C for the desired length of time. A rapid rate of reaction was obtained when the ratio of diazomethane to silk was about 1:5. This is four to five times the amount required to completely methylate the fibroin. This concentration may be maintained approximately by distilling more diazomethane into flask *A* as the reaction proceeds. After the treatment, the silk was removed and the excess ether and diazomethane were allowed to evaporate. The samples were thoroughly washed in successive portions of distilled water to remove the remaining organic solvents and then allowed to dry.

III. RESULTS AND DISCUSSION

1. REACTION OF SILK WITH DIAZOMETHANE

The extent of methylation of the tyrosine hydroxyl groups of the silk was determined by analysis of the treated material for tyrosine. The results in table 1 show the tyrosine contents of samples treated for different lengths of time. The rate of reaction is quite rapid at first, and gradually decreases as the treatment is continued. In 10 hours, 80 percent of the total tyrosine is converted into the methyl derivative. Treatments for longer periods of time, during which the concentration of diazomethane was kept nearly constant, resulted in a slight further decrease in tyrosine content. The rate of reaction may, in part, depend on penetration of the reagent into the fiber, and it might accordingly be expected that those groups on and near the surface would be methylated most rapidly. No appreciable decrease in tensile strength of the fibers occurred even on prolonged treatment. Since practically all of the tyrosine in silk is so readily methylated under these conditions, it appears that the hydroxyl groups of this amino acid are free in the untreated fiber.[3] A possible explanation of the discrepancy between this conclusion and that of the experiments with Folin's phenol reagent, previously described, might be found in a consideration of the nature of the reaction in the Folin method. This reaction depends on the oxidation of a phenolic hydroxyl group by the reagent, the latter in turn being reduced to the highly colored state. The depth of color developed by a known amount of tyrosine is used as a standard. If, however, the oxidation potential of the hydroxyl group of the tyrosine, as it exists in the protein, is different from that of the tyrosine itself, then the apparent tyrosine values obtained for the protein will not be true values. On this assumption, it would appear that the oxidation potential of the hydroxyl group is greater when the tyrosine is part of the protein molecule.

[3] It is of interest to note that the tyrosine contents of silk sericin, crystalline pepsin, and wool were reduced from 6.3, 7.8, and 5.8 percent to 0.5, 1.8, and 1.4 percent, respectively, after treatment for 20 hours with diazomethane.

TABLE 1.—*Tyrosine and methoxyl contents of silk fibroin after treatment for different lengths of time with an ethereal solution of diazomethane*

Duration of treatment	Tyrosine content	Methoxyl content of—		
		Fibroin	Hydrolysate	Hydrolysate (calculated from decrease in tyrosine content)
hr	%	%	%	%
0	12.1			
1	6.6	0.92	0.94	0.94
1.5	4.1	1.94	1.49	1.37
3	3.6	1.97	1.54	1.45
5	3.2	1.99	1.52	1.52
10	2.4	2.32	1.60	1.66
20	2.3	2.35	1.58	1.68
35	2.0	2.55	1.76	1.73
50	1.6	2.62	1.86	1.80

An examination of the data in columns 3 and 5 of table 1 shows that the methoxyl content of the treated silk is greater than can be accounted for, if it is assumed that only the hydroxyl groups of the tyrosine had reacted. Presumably, the "extra" methoxyl results from the reaction of diazomethane with other groups in the fiber. Conceivably, diazomethane might react with silk in several ways, as shown in the following equations:

$$P-CH_2-C_6H_4OH+CH_2N_2\rightarrow P-CH_2C_6H_4OCH_3+N_2 \quad (1)$$

$$P-CH_2NH_2+CH_2N_2\rightarrow P-CH_2NHCH_3+N_2 \quad (2)$$

$$P-CH_2COOH+CH_2N_2\rightarrow P-CH_2COOCH_3+N_2 \quad (3)$$

$$P-CH_2OH+CH_2N_2\rightarrow P-CH_2OCH_3+N_2, \quad (4)$$

where, P represents the protein molecule to which the above groups are attached. The equations then represent the reaction of diazomethane with (1) the hydroxyl groups of tyrosine, (2) the free amino groups, (3) the free carboxyl groups, and (4) the hydroxyl groups of serine.

Reaction (1) is shown to occur by the decrease in tyrosine content of the treated silk. Reaction (2) would result in the formation of a methylamino compound which would not give methoxyl under the analytical conditions used, and would therefore not account for any "extra" methoxyl. Moreover, amino-nitrogen determinations as shown in table 2 indicate that this reaction does not occur. Reaction (3) undoubtedly occurs since diazomethane is known to readily methylate carboxylic acids with the formation of methyl esters. Upon hydrolysis of the fibers under the conditions generally used in the tyrosine determination (6 *N* NaOH for 20 hours at 105° C), such esters would be expected to decompose liberating methyl alcohol with the regeneration of the carboxylic acid. The former would be evolved, and thus the methoxyl content of the hydrolysate should represent those methoxyl groups which resist the hydrolytic conditions used in these experiments. Reactions (1) and (4) would give this type of methoxyl.

TABLE 2.—*Total and amino-nitrogen contents of silk after treatment for different lengths of time with diazomethane*

Duration of treatment	Total N	Amino N
hr	%	%
0 (untreated)	18.78	0.10
20	[a] 18.82	.10
50	[a] 18.81	.10

[a] Corrected for increase in weight due to the addition of methyl groups.

The methoxyl contents of the hydrolysates are shown in column 4 of table 1. As was expected, the values are lower than those obtained for the treated silk (column 3). The agreement of the hydrolysate values with the methoxyl values calculated from the decrease in tyrosine contents (column 5), however, leaves little likelihood that reaction (4) occurs to any appreciable extent, especially since complete methylation of the serine of silk (1.8 percent [13]) would yield 0.53 percent of methoxyl groups, or about 30 percent of the total found.

The liberation of methyl alcohol from methylated silk during hydrolysis was readily demonstrated by refluxing several different samples for 1 hour with 0.1 *N* NaOH, and then distilling about half the solution into a receiver maintained at 0° C (to avoid loss of CH_3OH). The methyl alcohol content of the distillate was determined colorimetrically by Beyer's method. The results, calculated as methoxyl, are shown in table 3.

TABLE 3.—*Effect of a 1-hour treatment with a boiling 0.1 N solution of sodium hydroxide on the methoxyl content of methylated silk*

Duration of diazomethane treatment	Total methoxyl content	Methoxyl liberated during hydrolysis as methyl alcohol	Residual methoxyl content of silk
hr	%	%	%
3	1.97	0.30	1.55
10	2.32	.50	1.85
50	2.62	.73	2.08

If it is tentatively assumed that the "extra" methoxyl in the treated silk is in the form of esterified carboxyl groups, the present results indicate that silk fibroin contains an appreciable quantity of dicarboxylic amino acids, though this seems not to have been reported in the literature. From the data in table 1, it is estimated, on the basis of the above assumption, that silk may contain as much as 0.26 millimole per gram of free acidic groups. Such an appreciable amount of acidic groups would be expected to considerably influence the acidic and basic properties of the silk, and it should be readily detectable in the titration curve of the fiber.[4]

During these studies it was observed that an appreciable quantity of alkali was liberated when the fibroin was washed with water subsequent to the diazomethane treatment. A possible explanation for this is that cations, held by the acidic groups of the fiber, are freed as

[4] The titration curve of silk is now being determined as part of a separate investigation in progress in this laboratory.

these groups react with diazomethane. Since the reaction was carried out in ethereal solution, the alkali was not removed from the fibers until they were washed with water. If such an explanation is correct, no alkali should be liberated from ash-free silk under similar conditions. Furthermore, the rate of reaction of ash-free silk with diazomethane might be very different than that of the untreated silk, since at least a portion of the acidic groups of the latter would already be combined with inorganic substances.

In order to test this explanation and its consequences, a sample of ash-free fibroin was prepared by electrodialysis and then treated with diazomethane for different lengths of time. It was found that no measurable quantity of alkali was liberated when the treated sample was washed with water. Furthermore, the rate of increase in methoxyl content of the electrodialyzed silk during the first hour of treatment was greater than that of the untreated fibers, as shown by the results plotted in figure 2. After one hour of treatment, no "extra"

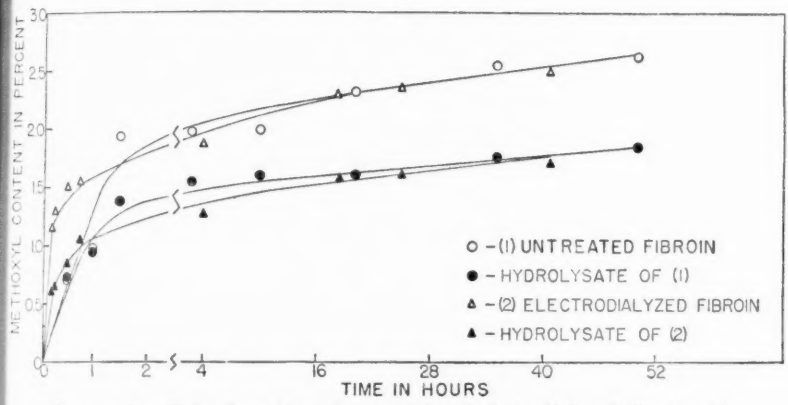


FIGURE 2.—*Rate of reaction of untreated and electrodialyzed fibroin with diazomethane.*

methoxyl was found in the latter, whereas treatment of the electrodialyzed fibers for the same length of time resulted in the formation of about 65 percent of the maximum "extra" methoxyl. After about 20 hours, there was no further increase in "extra" methoxyl content. As in the case of the untreated silk, the difference between the total and hydrolysate methoxyl contents of the electrodialyzed sample becomes approximately constant and equal to about 0.26 millimole per gram.

Although no further work on this phase of the investigation has been done, it appears from the rate studies that the specificity of diazomethane for the hydroxyl groups of tyrosine might be increased by appropriate pretreatment of the protein with some inorganic substance for the purpose of blocking the carboxyl groups.

2. REACTION OF METHYLATED SILK WITH NITROUS ACID

The methylated and untreated samples of silk were found to behave quite differently toward nitrous acid. The untreated silk assumed the usual dark-brown color, while the depth of color formed in the diazo-

methane-treated sample appeared to be dependent on the extent of methylation. A sample in which the tyrosine content had been reduced to a very low value was colored only slightly by nitrous acid.

Philpot and Small [14] have suggested that the color resulting from the reaction of pepsin with nitrous acid may be due to a nitrosation of the tyrosine, and that the first product of the reaction is an ortho-nitroso derivative. Assuming a similar reaction for silk, it appears that the methylation of the tyrosine prevents the formation of this derivative, either by decreasing the reactivity of the ortho position, or by preventing reaction of the nitrous acid with the free hydroxyl group to form a compound which subsequently rearranges to the ortho position. Regardless of which of the above mechanisms prevails, the difference in the behavior of methylated and untreated silks toward nitrous acid may be considered additional evidence that hydroxyl groups of the tyrosine in untreated silk are free.

IV. REFERENCES

[1] Folin and Ciocalteu, J. Biol. Chem. **73,** 627 (1927).
[2] Fruton and Lavin, J. Biol. Chem. **130,** 375 (1939).
[3] Abderhalden and Brockmann, Biochem. Z. **226,** 209 (1930).
[4] Abderhalden and Brockmann, Biochem. Z. **211,** 395 (1929).
[5] Kise and Carr, Textile Research **7,** 103 (1936).
[6] Carr, Textile Research **8,** 125 (1938).
[7] Herzig and Landsteiner, Biochem. Z. **61,** 458 (1914).
[8] Lugg, Biochem. J. **31,** 1422 (1937); **32,** 775 (1938).
[9] Rutherford, Harris, and Smith, J. Research NBS **19,** 467 (1937) RP1038.
[10] Vieböck and Brecker, Ber. deut. chem. Ges. **63B,** 3207 (1930).
[11] Beyer, J. Assoc. Official Agr. Chem. **22,** 151, (1939).
[12] Adamson and Kenner, J. Chem. Soc. **1935,** 286.
[13] Abderhalden, Z. physiol. Chem. **120,** 207 (1922).
[14] Philpot and Small, Biochem. J. **32,** 534, 542 (1938).
[15] Marshall and Acree, Ber. deut. chem. Ges. **43,** 2324 (1910).

WASHINGTON, August 14, 1940.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1339

Part of Journal of Research of the National Bureau of Standards, Volume 25, October 1940

CALIBRATION OF THERMOCOUPLES AT LOW TEMPERATURES

By Russell B. Scott

ABSTRACT

Descriptions are given of apparatus and methods used at the National Bureau of Standards for the calibration of thermocouples between 0° and −190° C. Descriptions are given of (1) a cryostat for maintaining very constant temperatures in the range 0° C to −170° C, (2) a convenient and accurate procedure for the realization of the equilibrium sublimation temperature of carbon dioxide using commercial solid CO_2, (3) a method of preparing pure oxygen for vapor-pressure thermometers, and (4) an improved apparatus for calibrating resistance thermometers and thermocouples at the oxygen boiling point. A reference table for copper-constantan thermocouples is given. Curves are shown representing the deviations from the table of a number of thermocouples calibrated at the National Bureau of Standards. These curves, which represent the behavior of a number of thermocouples from different sources, constitute the basis for a discussion of the relation between the accuracy obtainable with a copper-constantan thermocouple and the number and positions of the calibration points.

CONTENTS

	Page.
I. Introduction	459
II. Calibration by comparison with a platinum resistance thermometer	460
III. Reference table for copper-constantan thermocouples	463
IV. Calibration at fixed points	466
1. CO_2 point	466
2. Oxygen boiling point	469
V. Accuracy obtainable with copper-constantan thermocouples	472
VI. Summary	474

I. INTRODUCTION

Although the platinum resistance thermometer is used to define the International Temperature Scale in the range 0° to −190° C, copper-constantan thermocouples are also extensively used for temperature measurements in this range. A thermocouple may be calibrated either by direct comparison with a standard platinum resistance thermometer at several temperatures, or by determining its electromotive force (emf) at a number of fixed points, the temperatures of which are known on the International Temperature Scale. After having obtained values for the emf and temperature at a number of calibration points, the process of interpolating, to obtain a continuous temperature-emf relation over the whole range, is greatly facilitated by the use of a table giving the emf of a representative thermocouple. Such a table for a copper-constantan thermocouple is given in this paper. It is the purpose of this paper to describe, first, the apparatus and methods used at this Bureau to calibrate thermocouples by direct comparison with a platinum resistance ther-

mometer, and then to show how, with considerably simpler apparatus, certain fixed points may be used to obtain a calibration of sufficient accuracy for most purposes.

II. CALIBRATION BY COMPARISON WITH A PLATINUM RESISTANCE THERMOMETER

The strain-free platinum resistance thermometer is used as the standard temperature-measuring instrument for the calibration of thermocouples in the range 0° to —190° C, although at temperatures near the normal boiling point of oxygen (—182.97° C) the oxygen vapor-pressure thermometer may be used. At the low end of this range a bath of liquid air or liquid oxygen boiling at atmospheric pressure is used to cool a copper comparison block into which the thermocouple junction and the standard thermometer are inserted. For calibrations in the temperature range above —170° C, a cryostat[1] which automatically maintains the desired constant temperature in a stirred liquid bath is used. A vertical section of the cryostat is shown in figure 1. The refrigeration is supplied by liquid air in the outer Dewar flask, *C*, and controlled by varying the gas pressure between the walls of the inner Dewar, *D*, which contains the constant-temperature bath. This method of applying and controlling the refrigeration has been used by Rothe[2] and by Keyes, Taylor, and Smith.[3] The gas pressure is adjusted through tube *M*, which connects with a high-vacuum system.

The cryostat liquid is circulated by a propeller, *I*, which revolves in the bottom of a Bakelite tube, *P*, in such a direction that the liquid passes up through the inside of the Bakelite tube and down the outside. To permit this circulation, four windows, *B*, 2.5 cm long, were cut in the Bakelite tube. In order that the liquid at the surface shall be drawn away as its temperature is changed by the heat conducted in from the warm exterior, the liquid level is kept below the top of the windows. The propeller is driven at a speed of about 400 revolutions per minute by a system of three gears, *H*, driven by a shaft, *K*, connected to a motor through a flexible shaft, *O*. Three vertical vanes, *F*, support the bearings for the propeller and idler-gear shafts, and improve the circulation by preventing a whirling motion of the liquid above and below the propeller. Stainless-steel pinions and a Bakelite idler gear were found to be satisfactory. Monel-metal shafts turning in high-lead (85 percent) babbitt bearings were used. Since the cryostat liquids are poor lubricants, powdered graphite was rubbed on the bearing surfaces before assembling the stirrer. Special bearing materials consisting of a mixture of graphite in metal may be more satisfactory.

The heating coil, *J*, shown by dotted lines, is made of No. 22 AWG Ni-Cr alloy wire (80 Ni-20 Cr) and has a resistance of about 30 ohms. The bare wire is wound bifilarly on a form which fits the stirrer tube, *P*, its ends terminating at the top in leads, *Q*, which connect to the power supply through the thermoregulator. The form is made from a Bakelite tube by cutting wide slots in its walls, leaving six strips about 1 cm wide and supporting rings at the ends and center. Lag in the heater is reduced by this support and manner

[1] Scott and Brickwedde, BS J. Research **6**, 401 (1931) RP284.
[2] Rothe, Z. Instrumentenk. **22**, 14 (1902).
[3] Keyes, Taylor, and Smith, J. Math. Phys. **1**, 211 (1922).

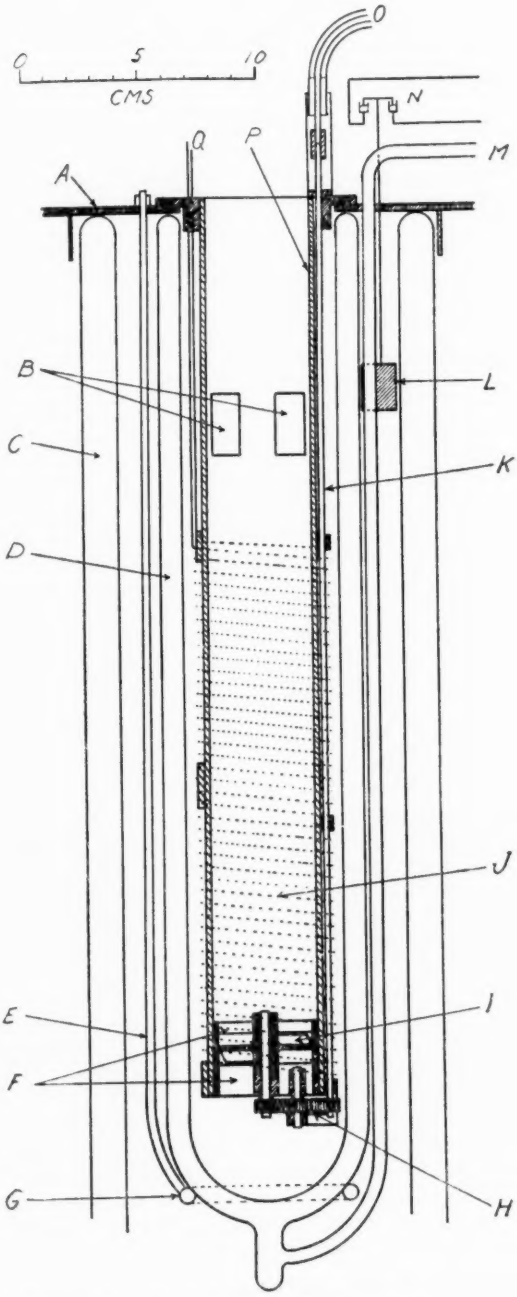


FIGURE 1.—*Vertical section of the cryostat.*

of winding which separates the heater coil from the tube, P, and allows the bath liquid to circulate on all sides of the wire. It is advantageous, in compensating for an excess of refrigeration, to have the heating surface close to and distributed over the refrigerating surface.

The thermoregulator consists of a coil of bare platinum wire immersed in the bath just above the propeller, and connected to a Wheatstone bridge as a three-lead, Siemens type, resistance thermometer. The mirror of the galvanometer in the Wheatstone-bridge circuit reflects a beam of light from an incandescent lamp, forming an image of the filament on the edge of a screen placed just in front of a photoelectric cell. If the bath is too cold, the image moves on to the sensitive plate of the photo cell; if too warm, it moves off.

When the cell is illuminated, the photoelectric current, amplified, actuates a relay which short circuits a variable external resistance, in series with the heating coil in the cryostat, increasing the heating current. The potential difference across the heater circuit is adjusted so that when the relay contacts are open, the bath is slowly cooling, and when they are closed, the bath temperature is slowly rising. The sensitivity of the thermoregulator may be increased almost without limit by increasing the current through the Wheatstone-bridge circuit, which contains the platinum resistance element. The constancy of the temperature of the bath, therefore, is not limited by the sensitivity of the thermoregulator. However, the finite time required for the temperature of the bath to respond to the demand of the thermoregulator causes the temperature to oscillate slightly about the mean. The amplitude of these oscillations may be made small by adjusting the heating current so that only a small increment is controlled by the thermoregulator. This increment must be large enough to take care of irregularities of heat conduction into the bath. It is not difficult to adjust the apparatus to maintain a temperature constant to $\pm 0.005°$ C, and by careful manipulation, the oscillations may be made smaller than $\pm 0.001°$ C. In some photoelectric thermoregulator circuits, thyratron tubes are used instead of mechanical relays. The thermoregulator described here was put into operation before thyratrons came into general use. It is possible that this circuit may, with profit, be modified to include a thyratron which controls the heating current, although the present arrangement appears to be entirely satisfactory for the calibration of thermocouples.

As far as possible, the nonflammable mixtures recommended by Kanolt [4] are used for the cryostat liquid. For temperatures down to $-75°$ C, the liquid used is the eutectic mixture of carbon tetrachloride and chloroform (49.4 percent by weight of CCl_4 and 50.6 percent of $CHCl_3$), which has a freezing point of $-81.4°$ C, as determined by Kanolt. For temperatures between $-75°$ and $-140°$ C, a five-component mixture containing 14.5 percent of chloroform, 25.3 percent of methylene chloride, 33.4 percent of ethyl bromide, 10.4 percent of *trans*-dichloroethylene, and 16.4 percent of trichloroethylene was used. This mixture freezes at about $-150°$ C.

[4] C. W. Kanolt, BS Sci. Pap. **20**, 619 (1924-26) S520.

At temperatures below −140° C the nonflammable liquids are so viscous that they cannot be readily stirred. For this lower range the liquid used is commercial propane, which is sold for domestic gas heating under various trade names. The propane, which is a gas at atmospheric pressure and room temperature, is compressed into steel cylinders and liquefied at a pressure of about 150 lb/in.^{2} It may be conveniently liquefied at atmospheric pressure by running it through a copper coil immersed in liquid air. Its boiling point is about −44° C, and it remains liquid down to liquid-air temperatures. It is, however, highly flammable, and its use is attended with some danger. Every precaution should be taken to prevent the mixing of liquid air and propane in case the Dewars break. The inner Dewar should be fitted with either a metal liner or a metal jacket if propane is used. If liquid nitrogen is available, it should be used instead of liquid air for the refrigerating liquid.

For the measurement of the emf of the thermocouple a low-range Wenner potentiometer is used. This instrument has two ranges: 0 to 11,000 μv, in steps of 0.1 μv; and 0 to 110,000 μv, in steps of 1 μv. Switches are provided for reversing simultaneously the potentiometer current and the emf being measured, so as to cancel out spurious emfs in the galvanometer circuit. Also, the leads from the potentiometer to the thermocouple may be shorted at the ice junctions to check the measuring circuit at zero emf.

III. REFERENCE TABLE FOR COPPER-CONSTANTAN THERMOCOUPLES

It has been found that the temperature-emf relation for a copper-constantan thermocouple, in the range 0° to −190° C, may be expressed by the equation

$$E = at + bt^2 + ct^3,$$

where E is the emf, t the temperature in degrees centigrade, and a, b, and c constants. A thermocouple made of carefully selected wire was calibrated at approximately 10-degree intervals over this range of temperatures. The constants a, b, and c were computed by the method of least squares. The observed points deviate randomly from the equation so obtained, the average deviation being 0.6 microvolt. As a convenience in calibrating and using thermocouples, table 1 was computed, giving the emf, at 2-degree intervals, and table 2, giving the temperature at intervals of 50 microvolts. This permits an accuracy of interpolation of 0.1 microvolt. Calibrations are made by determining the emf at a few temperatures and plotting deviations from the table.

TABLE 1.—*Reference table for copper-constantan thermocouples*

Temperature	E	dE/dt	Temperature	E	dE/dt	Temperature	E	dE/dt
°C	μv	μv/°C	°C	μv	μv/°C	°C	μv	μv/°C
0	0.0		−66	2327.4		−130	4136.7	
		38.4			31.8			24.4
−2	76.8		−68	2391.0		−132	4185.5	
		38.2			31.6			24.1
−4	153.2		−70	2454.1		−134	4233.8	
		38.0			31.3			23.9
−6	229.2		−72	2516.7		−136	4281.5	
		37.8			31.1			23.6
−8	304.8		−74	2579.0		−138	4328.8	
		37.6			30.9			23.4
−10	380.1		−76	2640.8		−140	4375.6	
		37.4			30.7			23.1
−12	455.0		−78	2702.1		−142	4421.8	
		37.3			30.5			22.9
−14	529.5		−80	2763.1		−144	4467.6	
		37.1			30.2			22.6
−16	603.7		−82	2823.5		−146	4512.9	
		36.9			30.0			22.4
−18	677.4		−84	2883.6		−148	4557.6	
		36.7			29.8			22.1
−20	750.8		−86	2943.1		−150	4601.9	
		36.5			29.6			21.9
−22	823.8		−88	3002.3		−152	4645.6	
		36.3			29.3			21.6
−24	896.3		−90	3061.0		−154	4688.8	
		36.1			29.1			21.3
−26	968.5		−92	3119.2		−156	4731.4	
		35.9			28.9			21.1
−28	1040.3		−94	3176.9		−158	4773.7	
		35.7			28.7			20.8
−30	1111.8		−96	3234.3		−160	4815.4	
		35.5			28.4			20.6
−32	1182.8		−98	3291.1		−162	4856.6	
		35.3			28.2			20.3
−34	1253.4		−100	3347.5		−164	4897.2	
		35.1			28.0			20.1
−36	1323.6		−102	3403.4		−166	4937.3	
		34.9			27.7			19.8
−38	1393.4		−104	3458.9		−168	4976.9	
		34.7			27.5			19.5
−40	1462.8		−106	3513.9		−170	5015.9	
		34.5			27.3			19.3
−42	1531.8		−108	3568.4		−172	5054.5	
		34.3			27.0			19.0
−44	1600.4		−110	3622.5		−174	5092.5	
		34.1			26.8			18.7
−46	1668.6		−112	3676.1		−176	5129.9	
		33.9			26.6			18.5
−48	1736.3		−114	3729.2		−178	5166.9	
		33.7			26.3			18.2
−50	1803.7		−116	3781.8		−180	5203.3	
		33.5			26.1			17.9
−52	1870.6		−118	3834.0		−182	5239.1	
		33.3			25.8			17.6
−54	1937.2		−120	3885.6		−184	5274.4	
		33.0			25.6			17.4
−56	2003.3		−122	3936.8		−186	5309.2	
		32.8			25.4			17.1
−58	2068.9		−124	3987.5		−188	5343.4	
		32.6			25.1			16.8
−60	2134.2		−126	4037.8		−190	5377.1	
		32.4			24.9			16.6
−62	2199.0		−128	4087.5		−192	5410.2	
		32.2			24.6			
−64	2263.4							
		32.0						

TABLE 2.—*Reference table for copperco-nstantan thermocouples*

E	Temperature	dt/dE	E	Temperature	dt/dE	E	Temperature	dt/dE
μv	° C	° C/μv	μv	° C	° C/μv	μv	° C	° C/μv
0	0. 0		1800	49. 890		3600	109. 166	
		0. 02604			0. 02984			0. 03718
50	1. 302		1850	51. 382		3650	111. 025	
		.02610			.02998			.03750
100	2. 607		1900	52. 881		3700	112. 900	
		.02620			.03014			.03780
150	3. 917		1950	54. 388		3750	114. 790	
		.02628			.03026			.03812
200	5. 231		2000	55. 901		3800	116. 696	
		.02636			.03042			.03846
250	6. 549		2050	57. 422		3850	118. 619	
		.02646			.03056			.03882
300	7. 872		2100	58. 950		3900	120. 560	
		.02654			.03072			.03916
350	9. 199		2150	60. 486		3950	122. 518	
		.02662			.03088			.03954
400	10. 530		2200	62. 030		4000	124. 495	
		.02672			.03104			.03992
450	11. 866		2250	63. 582		4050	126. 491	
		.02680			.03120			.04032
500	13. 206		2300	65. 142		4100	128. 507	
		.02690			.03136			.04072
550	14. 551		2350	66. 710		4150	130. 543	
		.02700			.03152			.04114
600	15. 901		2400	68. 286		4200	132. 600	
		.02708			.03170			.04156
650	17. 255		2450	69. 871		4250	134. 678	
		.02720			.03186			.04204
700	18. 615		2500	71. 464		4300	136. 780	
		.02728			.03206			.04250
750	19. 979		2550	73. 067		4350	138. 905	
		.02738			.03224			.04298
800	21. 348		2600	74. 679		4400	141. 054	
		.02748			.03242			.04350
850	22. 722		2650	76. 300		4450	143. 229	
		.02758			.03260			.04402
900	24. 101		2700	77. 930		4500	145. 430	
		.02768			.03280			.04458
950	25. 485		2750	79. 570		4550	147. 659	
		.02780			.03300			.04514
1000	26. 875		2800	81. 220		4600	149. 916	
		.02790			.03320			.04574
1050	28. 270		2850	82. 880		4650	152. 203	
		.02800			.03340			.04638
1100	29. 670		2900	84. 550		4700	154. 522	
		.02812			.03362			.04702
1150	31. 076		2950	86. 231		4750	156. 873	
		.02822			.03384			.04772
1200	32. 487		3000	87. 923		4800	159. 259	
		.02834			.03406			.04842
1250	33. 904		3050	89. 626		4850	161. 680	
		.02846			.03428			.04920
1300	35. 327		3100	91. 340		4900	164. 140	
		.02856			.03450			.04998
1350	36. 755		3150	93. 065		4950	166. 639	
		.02870			.03476			.05084
1400	38. 190		3200	94. 803		5000	169. 181	
		.02880			.03500			.05172
1450	39. 630		3250	96. 553		5050	171. 767	
		.02894			.03524			.05266
1500	41. 077		3300	98. 315		5100	174. 400	
		.02904			.03548			.05366
1550	42. 529		3350	100. 089		5150	177. 083	
		.02918			.03576			.05474
1600	43. 988		3400	101. 877		5200	179. 820	
		.02932			.03604			.05588
1650	45. 454		3450	103. 679		5250	182. 614	
		.02944			.03630			.05710
1700	46. 926		3500	105. 494		5300	185. 469	
		.02958			.03658			.05840
1750	48. 405		3550	107. 323		5350	188. 389	
		.02970			.03686			.05980
						5400	191. 379	

Deviation curves for a number of copper-constantan thermocouples are shown in figure 2. Each of these curves represents from 4 to 10 observed points. This is more points than are necessary for a calibration, but in this case closer spacing of the observations was needed so that irregularities in the deviation curves might be detected. Ordinates are emf of thermocouple minus emf from table 1. The observed emf is used as abscissa, because the deviation curves so obtained are more nearly linear than those obtained using abscissa to represent temperature. The deviation curves of thermocouples sent in for calibration are distributed almost equally above and below the axis. The curves are smooth, of slight curvature, and have no inflection points. Also shown in the figure are deviation curves of two other copper-constantan thermocouple tables, as given by Adams[4] and Southard and Andrews,[6] labeled *A* and *S*, respectively.

Adams' table was calculated from the equation

$$E=at-b\ (1-e^{-ct}),$$

the constants of which were determined by calibrations at the freezing point of mercury, the sublimation temperature of carbon dioxide, and the boiling point of oxygen. In view of the fact that when Adams' table was computed apparatus was not available for careful tests between the calibration points, his success is remarkable. It has been found, however, that most of the thermocouples calibrated at the National Bureau of Standards show somewhat more regular deviation curves from table 1 than from Adams' table. This is probably due to a difference in the composition of the constantan used by Adams, which affected the shape of the temperature-emf curve, and which had little effect on the magnitude of the emf produced. The table by Southard and Andrews was constructed from calibrations of a thermocouple at 15 temperatures between 0° and −190° C. The shape of the curve is almost the same as that represented by table 1, but the values of emf are considerably lower than the average of the thermocouples tested here. The thermocouple wires included in these tests range in size from No. 22 to No. 36 AWG, sizes which are ordinarily used at low temperatures.

IV. CALIBRATION AT FIXED POINTS

1. CO_2 POINT

The deviation curves of all the thermocouples that have been calibrated recently at the National Bureau of Standards are so nearly straight that a determination of the emf at the normal sublimation temperature of carbon dioxide (−78.51° C on the International Scale) is sufficient to establish the temperature-emf relation in the range 0° to −90° C. An accuracy of ±2 microvolts may be obtained by plotting the deviation curve in the manner shown in figure 2 and drawing a straight line through the observed point and the origin. Since solid carbon dioxide is now a widely distributed commercial product, many laboratories should find it useful as a means of realizing the normal sublimation temperature as a calibration point or as a check point for thermometers and thermocouples. However, certain

[4] *Symposium on Pyrometry* (A. I. M. M. E.) p. 165 (1920), Int. Crit. Tables **1**, 58 (1926).
[6] J. Franklin Inst. **207**, 323 (1929).

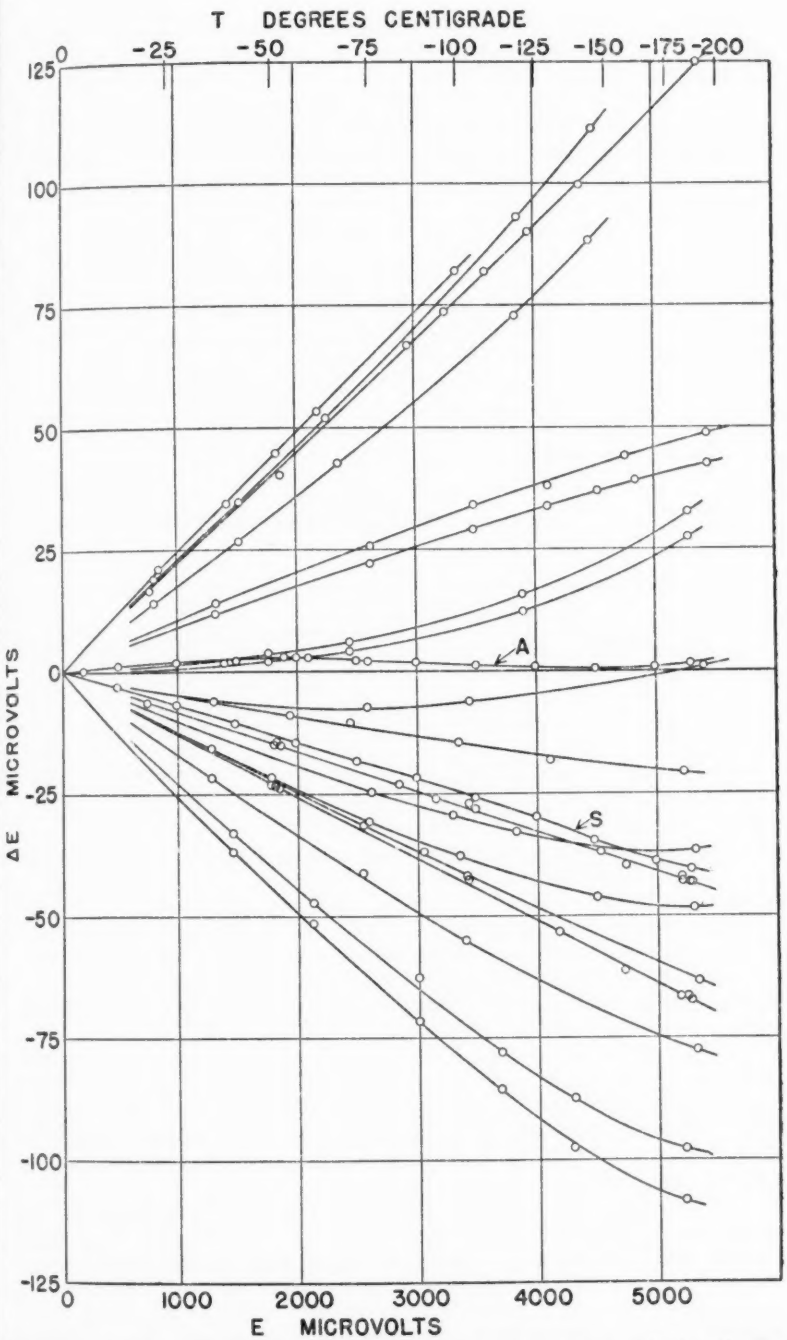


FIGURE 2.—*Differences between the calibrations of some copper-constantan thermocouples and the values given in table 1.*

precautions are necessary to obtain acceptable results. As solid carbon dioxide is usually handled, it is seldom surrounded by an atmosphere of pure CO_2 vapor, hence its temperature is considerably lower than the normal sublimation temperature. The temperature is that at which solid carbon dioxide has a vapor pressure equal to the partial pressure of the CO_2 vapor in the atmosphere immediately surrounding the solid. If a Dewar flask is filled with crushed solid CO_2, its initial temperature will be several degrees below the normal sublimation temperature. The temperature will rise slowly as the evaporated vapor washes out the air and, if diffusion of air into the flask is prevented, it will eventually reach the temperature at which the vapor pressure of CO_2 is equal to the pressure of the atmosphere. Figure 3 shows some measurements made with a platinum-resistance thermometer in such a bath.

It is common practice to use a mixture of solid CO_2 in a low-freezing liquid. J. and A. Zeleny [7] made measurements of the temperature of

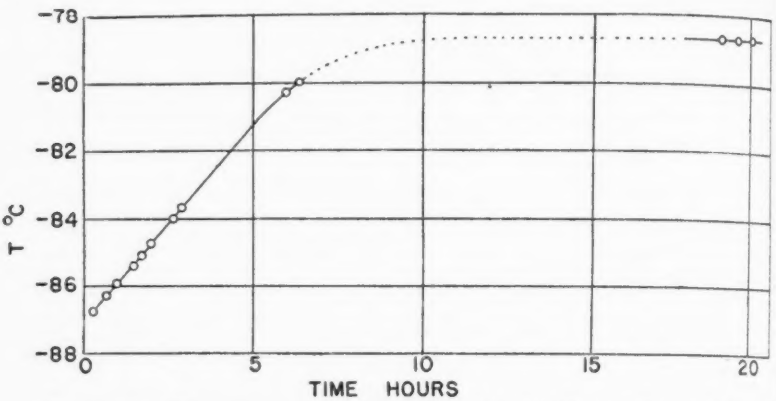


FIGURE 3.—*Temperature of crushed solid carbon dioxide in a Dewar flask.*

such baths, using solid CO_2 obtained by allowing liquid from a cylinder to escape and collecting the "snow" that is formed in the process. However, we have found that mixtures of crushed solid CO_2 and liquid do not behave very differently from solid CO_2 alone. That is, they all exhibit an initial low temperature and a gradual rise in temperature. Moreover, the equilibrium temperature of the mixture, at a point below the surface of the liquid, is affected by the hydrostatic pressure of the liquid at this point. Thus the temperature read by the thermocouple or thermometer depends upon the depth of immersion. Also, convection may cause disturbances in the temperature by transporting masses of liquid from one level to another having a different equilibrium temperature.

The quickest and most convenient method we have found is to use crushed solid CO_2 without a liquid, but with an electric heating coil buried in the solid CO_2, near the bottom of the Dewar flask and about 5 cm below the thermometers. An experiment with such an arrangement showed the following results. Starting at a temperature 6 degrees low, 30 watts in the heater caused the equilibrium temperature to be attained in 12 minutes. Further heating caused

[7] John Zeleny and Anthony Zeleny, Phys. Rev. [1] **23**, 308 (1906).

no change in temperature. The heat input was then reduced and left at 7 watts so as to keep a stream of CO_2 vapor flowing out of the flask to prevent air from diffusing in. Readings were then taken with two platinum-resistance thermometers in the bath, and with the barometer in the same room. The temperature of the solid carbon dioxide was calculated from its vapor pressure (barometric) by means the equation

$$\log_{10} p = 9.81137 - \frac{1349}{t+273.16},$$

where t is in degrees centigrade and p is in millimeters of Hg. The constants in this equation were chosen to fit the results of Meyers and Van Dusen [8] in the neighborhood of the normal sublimation temperature. The results are given in table 3. Other tests with just one thermometer have given similar results. From these results it appears that the temperature of equilibrium between solid and gaseous carbon dioxide may be attained by this method, with an accuracy of about 0.01°C. Judging from the evidence available, it appears unlikely that impurities found in commercial solid CO_2 will affect the temperature sufficiently to invalidate this conclusion.

TABLE 3.—*Sublimation temperature of* CO_2

Vapor pressure (barometric)	Temperature		
	Calculated by vapor-pressure equation	Resistance thermometer I	Resistance thermometer II
mm Hg	°C	°C	°C
754.44	−78.604	−78.598	−78.593

2. OXYGEN BOILING POINT

The deviation curves, figure 2, indicate that the boiling point of oxygen (−182.97° C), together with the sublimation point of CO_2, might be used to obtain a fair calibration curve for a copper-constantan thermocouple over the entire range of 0° to −190° C. However, the apparatus necessary for the realization of the oxygen boiling point is more elaborate than that used for the CO_2 point. Commercial oxygen usually contains enough nitrogen to make the boiling temperature uncertain. Even if the oxygen supply is pure, the liquid oxygen may become contaminated with atmospheric nitrogen by diffusion of air to the liquid surface. Also, the liquid may superheat, in which case the temperature of the liquid in the interior of the bath may be a degree or more above the temperature of the surface. Thus the temperature of a bath of liquid commercial oxygen cannot be determined simply by reading the barometer and applying a vapor-pressure equation, as was done in the case of solid carbon dioxide. A satisfactory method is to use a small quantity of pure oxygen in a vapor-pressure thermometer to determine the temperature of the bath.

It has been found that oxygen of sufficient purity for use in vapor-pressure thermometers may be prepared by the thermal decomposition

[8] C. H. Meyers and M. S. Van Dusen, *The vapor pressure of liquid and solid carbon dioxide*, BS J. Research 10, 381 (1933) RP538.

of potassium permanganate. The procedure was as follows: The salt was outgassed under high vacuum for 17 hours at a temperature of 160° to 175° C to remove adsorbed air. The temperature was then raised slowly while continuing the pumping until, in about 2 hours, the oxygen was coming off at a moderate rate at a temperature of about 215° C. After discarding the first oxygen generated at this temperature, the rest was collected by allowing it to condense into a bulb surrounded by liquid air. The collection was stopped when the salt reached a temperature of about 235° C.

A 4,500 cm^3 (gas) sample of oxygen thus obtained was distilled in a still with a rectifying column. The distillate was divided into 3 fractions of 300, 4,000 and 200 cm^3. The vapor pressures of these three fractions were compared in an apparatus equipped with a differential manometer filled with apiezon oil. The maximum difference observed was less than 0.02 mm Hg at −183° C. This indicates that there was no impurity present in the original sample in sufficient quantity to affect the vapor pressure appreciably. The vapor pressure of the oxygen prepared from potassium permanganate was also compared with that of a sample prepared by the electrolytic decomposition[9] of a carefully purified solution of barium hydroxide. It was necessary to use mercury manometers in this comparison, because the latter sample was sealed up in a vapor-pressure thermometer. The smallest detectable difference was, in this case, 0.1 mm Hg. No difference was observed.

Several designs of oxygen vapor-pressure thermometers and baths have been used in the various national standardizing laboratories. The following is a description of an arrangement now in use at the National Bureau of Standards. In figure 4, *F* is a massive copper cylinder immersed in a bath of liquid commercial oxygen. The oxygen from a high-pressure cylinder is liquefied by passing it through a coil of copper tubing immersed in liquid air. The copper cylinder is supported from above by the thin-walled (0.28 mm) Monel cylinder, *E*, which has openings in the sides to permit circulation of the liquid oxygen. The central cavity, *G*, contains a small quantity of pure liquid oxygen, prepared from $KMnO_4$ according to the method given above. The vapor pressure exerted by this pure oxygen is transmitted to the manometer, *A*, through the tube, *C*, which is an alloy of copper and nickel. The protecting tube, *D*, keeps the bath from coming in contact with the pressure-transmitting tube, *C*, so that cold spots on *C* are avoided. Thus the vapor pressure, as read by the manometer, is that which corresponds to the temperature of the copper cylinder, and it is not affected by a possible cold region near the surface of the bath. In order to prevent superheating of the bath, a slow stream of gaseous oxygen from a cylinder is admitted through tube, *B*, which extends to the bottom of the Dewar flask. The copper cylinder also contains wells into which thermocouples or resistance thermometers may be inserted. The copper-nickel tube, *C*, is connected to the Pyrex glass of the manometer by soldering it to the copper end of a Housekeeper[10] seal. The inside diameter of the manometer tubing is 1 cm. The positions of the mercury menisci are observed by means of a mirror-backed glass scale mounted in contact with the manometer tubes. The precision of measurement is about 0.1 mm. The

[9] Shepherd, Weaver, and Pickering, J. Research NBS **22**, 301 (1939) RP1182.
[10] J. Am. Inst. Elec. Eng. **42**, 954 (1923).

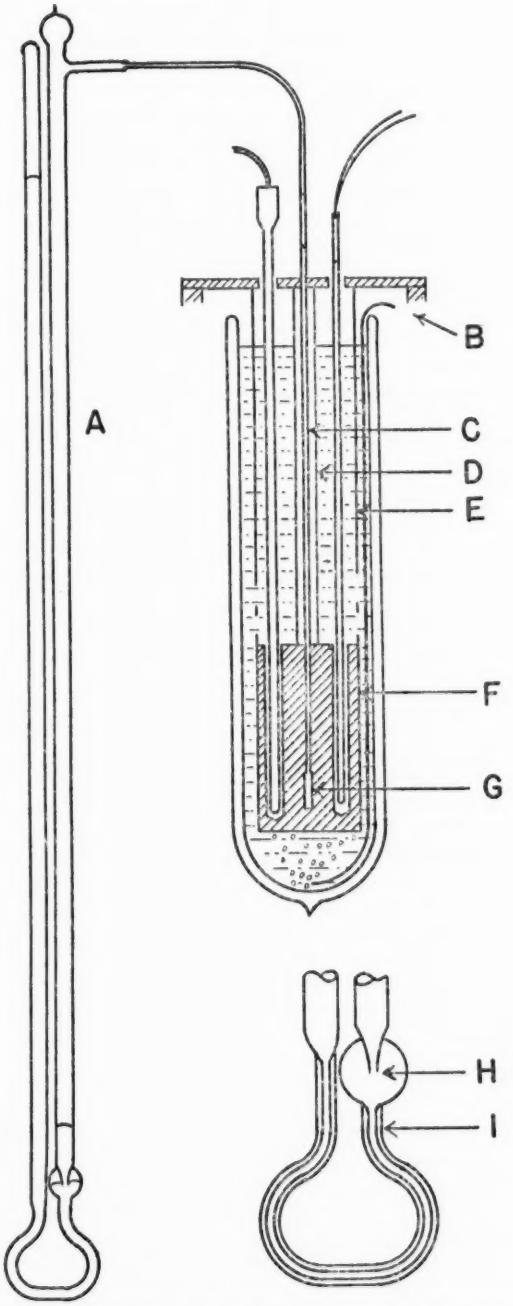


FIGURE 4.—*Apparatus for calibration of thermometers and thermocouples at boiling point of oxygen.*

amount of oxygen in the vapor-pressure bulb and manometer is such that when the copper cylinder is at room temperature the pressure is about 3 atmospheres. Thus the system, after being filled with pure oxygen, may be permanently sealed off.

Figure 4 (lower right) is an enlarged view of the bottom of the manometer. This illustrates a method of keeping the manometer clean on the oxygen side. In the usual type of manometer the oxidation of the mercury on the oxygen side darkens the tube and causes a misshapen meniscus, which introduces errors into the measurement of pressure. In this manometer, when the apparatus is not in use, the mercury meniscus stands in the small tube at *I*, presenting only a small surface to the oxygen. When the copper cylinder is cooled and oxygen condenses, the mercury rises and the surface spreads in the bulb so that, as the mercury flows into the manometer tube through the constricted tip, *H*, nearly all of the oxide is left behind. The ratio of the cross-sectional area of the bulb to that of the tip is about 100.

The results obtained with this apparatus show a considerable improvement over those obtained when using an all-glass vapor-pressure thermometer in a stirred bath of liquid oxygen. It is believed that oxygen-point calibrations of platinum-resistance thermometers may be made with a reproducibility of about $\pm 0.003°$ C. This, of course, greatly exceeds the accuracy needed for thermocouple calibrations.

V. ACCURACY OBTAINABLE WITH COPPER-CONSTANTAN THERMOCOUPLES

The accurancy with which copper-constantan thermocouples may be calibrated and used at low temperatures is usually limited by lack of homogeneity of the wires. That is, irregularities in the chemical composition or physical condition of the wires, in regions where temperature gradients exist, cause spurious emf to appear which are not determined by the temperature of the thermocouple junction. In the copper-constantan thermocouple the constantan is usually the element responsible for most of the spurious emf, the copper as a rule being relatively uniform. Specimens of constantan have been found in which emf as large as 10 microvolts appeared, when part of the wire was at liquid-air temperature and the rest at room temperature. By testing the wire and choosing pieces in which such effects are small, thermocouples may be constructed which are much more dependable than those made of untested wire. Another improvement that is sometimes used is to have several constantan wires in the same bundle, either in parallel, forming with the copper wire a single thermocouple, or in series with an equal number of copper wires, forming a multiple junction thermopile. In both of these arrangements effects of irregularities in the different wires will usually be partially canceled. For some purposes it is desirable to protect the thermocouple, or at least those portions of the wires subject to temperature gradients, with a rigid covering, so that handling will not set up strains in the wires. This arrangement, however, defeats one of the principal advantages of thermocouples, that is, their adaptability for use in an intricate apparatus from which the wires must be brought out through a devious path. A few thermocouples of special construction, in which several selected constantan wires were used,

have been calibrated at low temperatures at the National Bureau of Standards. Although experience with such thermocouples has not been extensive, it is believed that the best of these, when calibrated at intervals of 50° C or less, and used in conjunction with table 1, will give results which are in error by less than 1 microvolt. This limit of error is given on the basis of one thermojunction; for a multiple-junction instrument it will be larger. The effect of inhomogeneities in thermocouple wire, methods of testing the wire, the construction of multiple-junction thermocouples, and general technique of thermoelectric measurements have been treated in detail by White.[11] He is principally concerned with thermocouples for use in calorimetry at moderate temperatures, but a great deal of the technique is applicable to low-temperature work.

If the emf of a thermocouple is observed at three temperatures, about −70°, −140°, and −190° C, the deviation curve can, as a rule, be drawn so as not to be in error at intermediate temperatures, in the range 0° to −190° C, by as much as 2 microvolts. The relation

$$E=at+bt^2+ct^3,$$

with constants calculated from observed emf at the above temperatures, will give results almost as accurate, but the method of using table 1, together with a deviation curve, is to be preferred, both because it is more convenient, and also because any serious error of calibration is strikingly evident as an irregularity in the deviation curve.

If a thermocouple is to be used only in the range 0° to −90° C and an accuracy of ±2 microvolts is sufficient, a single calibration in subliming carbon dioxide is adequate. The deviation curve in this case is, of course, a straight line through the observed point and the origin. For most thermocouples a calibration accurate to ±2 microvolts is all that is justified, because inhomogeneities in the wires are likely to introduce larger errors.

If the thermocouple is calibrated at the oxygen boiling point, as well as at the CO_2 point, a temperature-emf relation, having a maximum error of less than 4 microvolts at temperatures between the CO_2 and oxygen points, may be obtained. The deviation curve should approximate a parabola, having its greatest curvature at the low-temperature end. If the deviation curve is found to be nearly linear, the maximum error will be considerably less than 4 microvolts. Wiebe and Brevoort[12] state that the deviation curve for a copper-constantan thermocouple calibrated at these two temperatures can be represented by the quadratic equation

$$\text{Deviation}=aE+bE^2,$$

with an accuracy of about 0.05° C (0.8 to 2.0 μv). Adams' table was used as the basis of reference. They base their conclusion on calibrations of seven thermocouples of their own and one from another laboratory. Their somewhat smaller limit of error may probably be explained by the fact that the constantan of their thermocouples was not obtained from as great a number of sources as that of the thermocouples sent to this laboratory for calibration, hence they did not find quite as great a variation in the shapes of the deviation curves.

[11] Walter P. White, J. Am. Chem. Soc. **36**, 2292 (1914): Rev. Sci. Instr. **4**, 142 (1933).
[12] Rev. Sci. Instr. **2**, 450, (1931).

A thermocouple used only at low temperatures should be expected to maintain its calibration better than one subjected to temperatures which accelerate physical and chemical changes in the metals. Giauque and Egan,[13] and Stephenson and Giauque[14] have checked some copper-constantan thermocouples several years after their original calibration. They find some discrepancies at temperatures between −190° and −260° C, but above −190°C no change in calibration of as much as 0.05° C was found. Aston[15] reports a somewhat similar experience, with evidence that the changes observed at very low temperatures were due to repeated cooling of the thermocouples. His results also indicate that, at temperatures above −200° C, a copper-constantan thermocouple will not change its calibration by more than 0.05° C over a period of several years.

VI. SUMMARY

Thermocouples sent to the National Bureau of Standards for calibration at low temperatures are compared with a standard platinum-resistance thermometer in a bath of uniform and constant temperature. The emf-temperature relation over an extended range is obtained by measuring the emf at a few selected temperatures and plotting the deviations from the values in a standard table. Deviation curves of a number of copper-constantan thermocouples from different sources indicate that, if the demand for accuracy is not too exacting, two points, the CO_2 sublimation temperature and the oxygen boiling point, may be used to obtain a calibration covering the range 0° to −190° C. Thus a fair calibration may be obtained even though a platinum-resistance thermometer and its accessory apparatus are not available. Furthermore, the apparatus used to attain the fixed temperature is not complicated. This is particularly true of the apparatus and material required for the CO_2 points. Ordinary commercial solid carbon dioxide is used, and the apparatus consists of a Dewar flask, an electric heating coil, and a barometer for determining the pressure. This calibration at the temperature of subliming CO_2 is sufficient to establish the temperature-emf relation from 0° C to −90° C with an accuracy of ±2 microvolts. It should be remembered that unless considerable care is taken in selecting the constantan wire, errors due to inhomogeneity may be larger than errors of observation. Thus the quality of the thermocouples may not justify the highest accuracy of calibration, and the simpler method of using one or two fixed points may be entirely adequate.

WASHINGTON, July 13, 1940.

[13] J. Chem. Phys. **5**, 45 (1937).
[14] J. Chem. Phys. **5**, 149 (1937).
[15] Abstracts of papers presented at the meeting of the Am. Chem. Soc. at Boston, Mass., September 11 to 15, 1939. Published by the Division of Physical and Inorganic Chemistry.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1340

Part of Journal of Research of the National Bureau of Standards, Volume 25, October 1940

STUDIES ON THE SYSTEM LIME-FERRIC OXIDE-SILICA

By Milton D. Burdick

ABSTRACT

The equilibrium diagram of a part of the ternary system lime-ferric oxide-silica is presented. A comparison with the diagram of the lime-alumina-silica system shows that the presence of ferric oxide results in extension of the stability fields of the calcium silicates and the lowering of the liquidus and eutectic temperatures in much of the area investigated. Evidence from thermal analyses is offered of a limited solid-solution series between dicalcium silicate and ferric oxide, substantiated by an X-ray investigation. The amount of reduction of ferric oxide at the liquidus temperature of representative ternary mixtures is recorded. The applications to iron-rich cements are discussed.

CONTENTS

	Page
I. Introduction	475
II. Experimental methods	476
III. Stability fields	476
1. SiO_2	476
2. $CaO.SiC_2$	477
3. $3CaO.2SiO_2$	479
4. $2CaO.SiO_2$	480
5. $3CaO.SiO_2$	484
6. CaO	485
IV. Reduction of ferric oxide in ternary mixtures	485
V. Applications	486
VI. Summary	487
VII. References	488

I. INTRODUCTION

The system lime-ferric oxide-silica is one of the ternary systems involving the major oxide components of portland cement which has not been thoroughly investigated. Further study of this system seemed desirable, since it might be applicable to high-iron cements, and because it would supply preliminary information necessary for an investigation of the quaternary system, CaO-Al_2O_3-Fe_2O_3-SiO_2, in the region of aluminous cements. In this study the phase relations have been determined in that portion of the system including from 15 percent to 65 percent of CaO and up to 65 percent of Fe_2O_3.

Previous investigators of a part of the system covered in this report [1] [1] noted the presence of a stability field for the compound tricalcium silicate, reported no ternary compounds, and observed the inability of ferric oxide to prevent the β-γ inversion of dicalcium silicate, except when present in high concentration. These findings are confirmed by the present study.

Two of the binary systems making up the ternary system under consideration have been investigated. These are the systems

[1] Numbers in brackets indicate the literature references at the end of this paper.

CaO-SiO_2 [2, 3, 4, 5] and CaO-Fe_2O_3 [6]. The binary system Fe_2O_3-SiO_2 has not been thoroughly studied, but an equilibrium diagram has been suggested [7].

In the determination of the primary and secondary phases of all preparations containing more than 30 percent of ferric oxide, liquids were developed with a sufficient concentration of ferric oxide to cause the persistent development of quench growths of calcium ferrites.

II. EXPERIMENTAL METHODS

Calcium carbonate, purified silica gel, and ferric oxide were the materials from which the mixtures studied were prepared. The calcium carbonate was of reagent quality for alkali determinations. Analyses showed 55.94 percent of CaO, 0.04 percent of SiO_2, 0.02 percent of R_2O_3, 0.02 percent of MgO, and 44.03 percent was ignition loss. The silica gel was a commercial granular product, which was purified by boiling with concentrated nitric acid and subsequently thoroughly washed and dried. Treatment with hydrofluoric and sulfuric acids left an insoluble residue of 0.08 percent, based on the weight of the ignited silica, composed of 5 parts of Al_2O_3 and 3 parts of Fe_2O_3. The ferric oxide, by analysis, contained 0.40 percent of SiO_2, 99.28 percent of Fe_2O_3, and 0.24 percent was ignition loss.

The samples for study were prepared by weighing appropriate amounts of the materials, correcting for ignition loss and impurities, grinding and intimately mixing in an agate mortar, sintering twice in a platinum crucible with intermediate grinding, and finally regrinding. Analyses of three mixtures showed close agreement between calculated and analyzed compositions.

A vertical-tube platinum-wound resistance furnace and control [8] was used for the high-temperature treatments.

Temperatures were measured by means of platinum–platinum-rhodium thermocouples and a type *K* potentiometer and a suspension galvanometer. The single thermocouples were compared with a calibrated couple. The differential thermocouple used in the determination of heating curves was calibrated frequently at the melting point of potassium sulfate, 1,067° C, [18] and by determining the α-β inversion temperature of pure dicalcium silicate, 1,420° C [3].

Microscopic examination of the quenched samples was made with a petrographic microscope, and indices of refraction were measured by the immersion method.

III. STABILITY FIELDS

In figure 1 are shown the boundary lines of the primary phase areas. The stability fields of SiO_2, α-$CaO{\cdot}SiO_2$, $2CaO{\cdot}SiO_2$, and CaO are relatively large when compared with those of $3CaO{\cdot}2SiO_2$, $3CaO{\cdot}SiO_2$, and $2CaO{\cdot}Fe_2O_3$. The dots represent the mixtures investigated.

Isotherms have been inserted in figure 2 to show the temperatures of complete melting.

1. SiO_2

The data on preparations in which tridymite occurs as the primary phase in equilibrium with liquid are given in table 1.

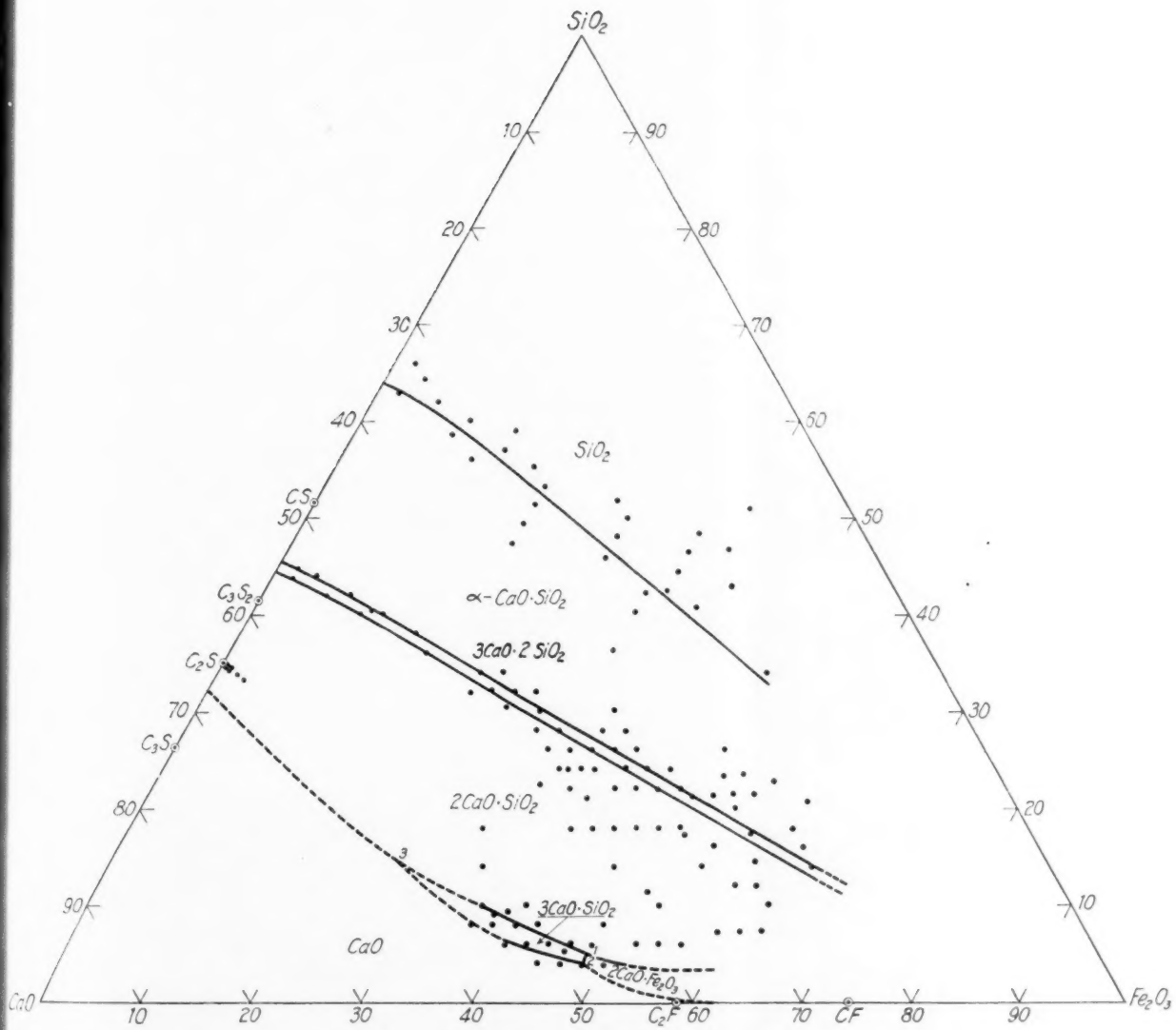


FIGURE 1.—*Triangular concentration diagram of a part of the system* $CaO\text{-}Fe_2O_3\text{-}SiO_2$, *showing the limits of the stability fields.* Dots represent the composition investigated.

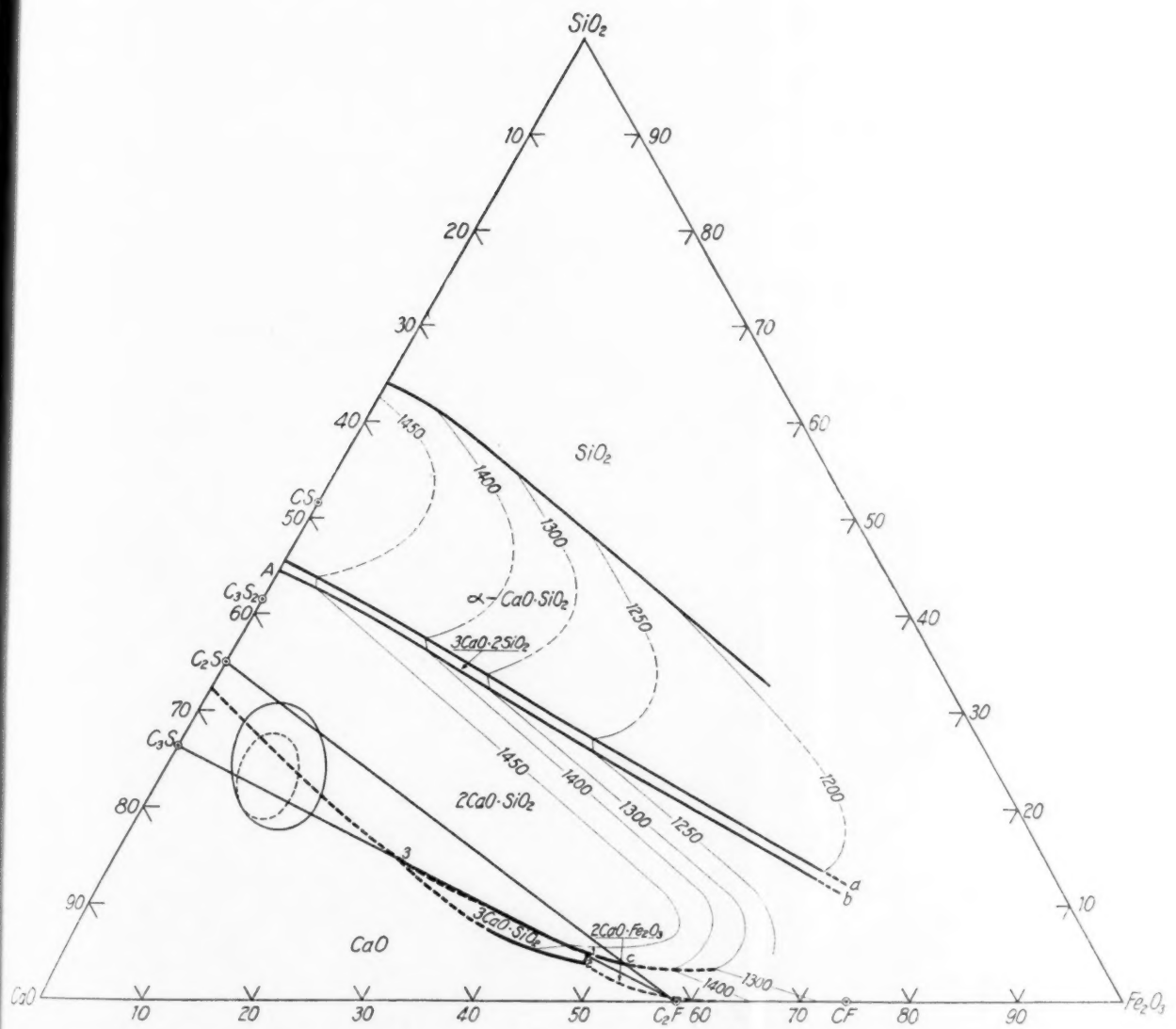


FIGURE 2.—*Triangular concentration diagram of a part of the system* $CaO\text{-}Fe_2O_3\text{-}SiO_2$ *with isotherms showing temperatures of complete melting and composition triangles.*

Preparations treated for periods of an hour or less at appropriate temperatures contained crystalline silica identified as tridymite by its index of refraction and its birefringence. The characteristic lath-like shapes [9] were observed only in those preparations treated for longer periods of time before quenching.

TABLE 1.—*Composition of and data on preparations determining the silica field*

Preparation number	Composition (percent by weight)			Time at constant temperature	Temperature	Phases (CS=CaO·SiO$_2$)
	Fe_2O_3	CaO	SiO_2			
	%	%	%	*hr*	°C	
1	1.8	32.1	66.1	16	1,439	SiO_2+glass.
2	3.7	32.1	64.2	½	1,465	Do.
				½	1,437	SiO_2+CS+glass.
3	6.0	32.0	62.0	½	1,408	SiO_2+glass.
				½	1,360	SiO_2+CS+glass.
4	10.0	30.0	60.0	¾	1,395	SiO_2+glass.
				1	1,360	SiO_2+CS+glass.
5	14.6	26.4	59.0	21	1,328	SiO_2+glass.
				¼	1,325	Do.
6	14.6	28.4	57.0	17	1,315	SiO_2+CS+glass.
				21	1,431	Glass only.
7	18.2	26.6	55.2	1	1,335	SiO_2+glass.
				½	1,280	Do.
8	20.1	26.6	53.3	½	1,258	SiO_2+CS+glass.
9	27.4	20.8	51.8	¼	1,291	SiO_2+glass.
10	29.2	20.9	49.9	¼	1,278	Do.
				2	1,248	Glass only.
11	29.2	22.9	47.9	2	1,231	SiO_2+glass.
				2	1,192	SiO_2+CS+glass.
12	36.5	15.1	48.4	¼	1,432	SiO_2+glass.
13	36.5	17.1	46.4	½	1,413	Glass only.
				½	1,323	SiO_2+glass.
				¼	1,324	Glass only.
14	36.5	19.1	44.4	1	1,306	SiO_2+glass.
				2	1,199	Do.
				2	1,176	SiO_2+CS+glass.
				2	1,243	Glass only.
15	36.5	21.1	42.4	2	1,216	SiO_2+glass.
				2	1,192	SiO_2+CS+glass.
16	40.1	13.2	46.7	½	1,402	SiO_2+glass.
17	40.1	9.2	50.7	2	1,509	Do.
18	40.1	19.2	40.7	2	1,342	Do.
				4	1,196	Do.
				2	1,176	SiO_2+CS+glass.
19	41.9	15.3	42.8	2	1,344	SiO_2+glass.
20	50.0	16.0	34.0	2	1,176	Do.
				2	1,154	SiO_2+CS+glass.

2. $CaO.SiO_2$

The data on preparations which determine the area within which pseudowollastonite (α-$CaO.SiO_2$) occurs as the primary phase are listed in table 2. Wollastonite (β-$CaO.SiO_2$) was not observed in any of the quenched samples, since few were held below 1,200° C and none below 1,150° C, which has been suggested as the true α-β inversion temperature of monocalcium silicate [10].

Iwase and Niskioka [11], in discussing the system $CaO.SiO_2$-$2CaO.Fe_2O_3$, have described this as a simple binary system. Their diagram shows $CaO.SiO_2$ and $2CaO.Fe_2O_3$ to be the only solid phases appearing on the liquidus curve with the eutectic at 45 percent $CaO.SiO_2$. Inasmuch as the compound $2CaO.Fe_2O_3$ melts incongruently, mixtures of this with any other compound or oxide should be defined as a pseudobinary system. Also, as can be seen from figure 2, a join between the compounds $CaO.SiO_2$ and $2CaO.Fe_2O_3$ would

cross the stability fields of $CaO.SiO_2$, $3CaO.2SiO_2$, $2CaO.SiO_2$, $2CaO.Fe_2O_3$, and CaO. The eutectic temperature, reported by the above investigators, for mixtures of $CaO.SiO_2$ and $2CaO.Fe_2O_3$ containing from 50 to 90 percent of $CaO.SiO_2$ has a mean value of 1,181° C. In the ternary system $CaO-Fe_2O_3-SiO_2$ the above mixtures are located in the composition triangle $CaO.SiO_2$, $3CaO.2SiO_2$, $CaO.Fe_2O_3$. Thermal analyses of preparations in this triangle, made during the current investigation, indicate a value of 1,188° C for the eutectic temperature. The few degrees between 1,188° C, as indicated by heating-curve breaks of preparations in the ternary system, and 1,181° C, as determined by Iwase and Niskioka from arrests of the cooling curves of pseudobinary mixtures, can easily be attributed to supercooling of the liquids in the latter case. Such a small amount of supercooling is unusual for a silicate system, and is attributable to the fluidity of the melts, which was noted by Sitz [12] to be greatest on the line $CaO.SiO_2$—$CaO.Fe_2O_3$. If Iwase and Niskioka's mixtures of $CaO.SiO_2$—$CaO.Fe_2O_3$ are plotted on the ternary diagram, the cooling-curve breaks, interpreted by them to indicate the melting point of the primary phase, are seen rather to indicate boundary temperatures, while the actual liquidus temperatures are, in some cases, as much as 200° C higher.

TABLE 2.—*Composition of and data on preparations determining the α-monocalcium silicate field*

Preparation number	Composition (percent by weight)			Time at constant temperature	Temperature	Phases (CS=$CaO.SiO_2$, C_3S_2=$3CaO.2SiO_2$)
	Fe_2O_3	CaO	SiO_2			
	%	%	%	*hr*	°C	
21	2.0	35.2	62.8	1½	1,434	CS+glass.
				½	1,417	CS+SiO_2+glass.
22	9.1	32.3	58.6	¼	1,411	Glass only.
				1	1,381	CS+glass.
23	12.0	32.0	56.0	¼	1,346	Do.
				¼	1,328	CS+SiO_2+glass.
24	10.0	36.0	54.0	¾	1,470	Glass only.
				¾	1,414	CS+glass.
				1	1,347	Do.
				1	1,261	CS+SiO_2+glass.
25	20.1	28.6	51.3	¾	1,329	Glass only.
				¾	1,287	CS+glass.
26	20.1	30.6	49.3	2	1,342	Glass only.
				1	1,332	CS+glass.
				1½	1,305	CS+SiO_2+glass.
27	20.1	32.6	47.3	½	1,408	Glass only.
				½	1,302	CS+glass.
28	29.2	24.9	45.9	2	1,215	Glass only.
				1½	1,196	CS+glass.
29	34.6	23.1	42.3	2	1,242	Glass only.
				2	1,217	CS+glass.
30	34.6	25.1	40.3	¾	1,262	Glass only.
				¾	1,244	CS+glass.
31	2.0	53.5	44.5	¼	1,459	Glass only.
				¼	1,456	CS+glass.
				¼	1,447	CS+C_3S_2+glass.
32	4.0	52.0	44.0	¼	1,471	Glass only.
				¼	1,450	CS+glass.
				¼	1,426	Do.
				¼	1,418	CS+C_3S_2+glass.
33	8.0	50.0	42.0	¼	1,460	Glass only.
				¼	1,450	CS+glass.
				¼	1,421	Do.
				¼	1,410	CS+C_3S_2+glass.
34	12.0	48.0	40.0	¼	1,442	Glass only.
				¼	1,429	CS+glass.
35	16.0	46.0	38.0	¼	1,412	Do.
				¼	1,372	CS+C_3S_2+glass.

TABLE 2.—*Composition of and data on preparations determining the α-monocalcium silicate field*—Continued

Preparation number	Composition (percent by weight)			Time at constant temperature	Temperature	Phases (CS=CaO.SiO$_2$ C$_2$S$_3$=3CaO.2SiO$_2$)
	Fe_2O_3	CaO	SiO_2			
	%	%	%	*hr*	°C	
36	26.0	40.0	34.0	¾	1,258	CS+glass.
				¼	1,220	CS+C_2S_2+glass.
37	28.0	40.0	32.0	¼	1,351	CS+glass.
				¼	1,320	CS+C_2S_2+glass.
38	30.0	38.0	32.0	¼	1,348	Glass only.
				¼	1,280	CS+glass.
				1	1,245	CS+C_2S_2+glass.
39	38.0	32.0	30.0	¼	1,265	Glass only.
				1	1,255	CS+glass.
40	38.0	34.0	28.0	¼	1,263	Glass only.
				1	1,251	CS+glass.
				1½	1,211	Do.
				1	1,196	CS+C_2S_2+glass.
41	40.0	32.0	28.0	¼	1,259	Glass only.
				¼	1,241	CS+glass.
42	40.0	34.0	26.0	¾	1,235	Glass only.
				1	1,218	CS+glass.
				1½	1,207	CS+C_2S_2+glass.
43	44.0	32.0	24.0	1	1,242	Glass only.
				2	1,235	CS+glass.
				1	1,230	CS+C_2S_2+glass.
44	46.0	30.0	24.0	½	1,302	Glass only.
				1	1,234	CS+glass.
				1	1,219	CS+C_2S_2+glass.
45	48.0	30.0	22.0	1	1,230	Glass only.
				hc[a]	1,228	Liquidus
				1	1,225	CS+glass.
				1	1,217	CS+C_2S_2+glass.
46	50.0	24.0	26.0	1	1,302	Glass only.
				1	1,250	CS+glass.
47	50.0	21.2	22.8	1	1,303	Glass only.
				1	1,277	CS+glass.
48	51.1	25.5	23.4	1	1,208	Do.
				2	1,202	CS+C_2S_2+glass.
49	51.1	27.5	21.4	2	1,209	CS+glass.
				1¾	1,204	CS+C_2S_2+glass.
50	52.9	25.6	21.5	2	1,213	CS+glass.
				2	1,199	CS+C_2S_2+glass.
51	60.0	19.2	20.8	1	1,275	CS+glass.
52	54.7	24.7	21.6	2	1,216	Do.
				2	1,201	CS+C_2S_2+glass.
53	60.2	21.8	18.0	1½	1,209	CS+glass.
				2	1,200	CS+C_2S_2+glass.
54	62.0	21.9	16.1	1½	1,201	CS+glass.
				1½	1,197	CS+C_2S_2+glass.

[a] hc indicates data obtained from heating curves. Under the column headed "Phases", the data given in such cases represent interpretations placed on breaks of heating curves.

3. $3CaO.2SiO_2$

The data on preparations which determine the area within which tricalcium disilicate is the primary phase are given in table 3. In many preparations rich in ferric oxide (table 2) the occurrence of $3CaO.2SiO_2$ as the second solid phase to appear on cooling indicates the existence of this field somewhat farther than is shown in the figures. Preparations treated for 1 hour or more before quenching showed large, well-formed crystals of the primary phase. In abutting fields in which $3CaO.2SiO_2$ occurred as the secondary phase, the crystals also formed easily and grew to large sizes.

TABLE 3.—*Composition of and data on preparations determining the tricalcium disilicate field*

Preparation number	Composition (percentage by weight)			Time at constant temperature	Temperature	Phases (C=CaO; S=SiO_2)
	Fe_2O_3	CaO	SiO_2			
	%	%	%	*hr*	°C	
55	2.0	54.0	44.0	¼	1,459	Glass only.
55 [a]	[b] 2.17	53.86	43.68	¼	1,455	C_3S_2+C_2S+glass.
				¼	1,446	C_3S_2+CS+glass.
56	10.8	48.8	40.4	¼	1,385	Glass only.
				¼	1,366	C_3S_2+glass.
				¼	1,348	C_3S_2+CS+glass.
57	24.0	42.0	34.0	¼	1,308	C_3S_2+glass.
				¼	1,270	C_3S_2+CS+glass.
58	26.0	42.0	32.0	¼	1,324	Glass only.
				1	1,282	C_3S_2+glass.
59	31.2	38.8	30.0	¼	1,269	Glass only.
				¼	1,248	C_3S_2+glass.
60	34.0	38.0	28.0	¼	1,233	Glass only.
				¼	1,231	C_3S_2+glass.
61	38.0	36.0	26.0	¼	1,240	Glass only.
				¼	1,231	C_3S_2+glass.
62	42.0	34.0	24.0	¼	1,236	Glass only.
				¼	1,230	C_3S_2+glass.
63	46.0	32.0	22.0	1	1,235	Glass only.
				¾	1,222	C_3S_2+C_2S+glass.
64	49.3	29.5	21.2	2	1,218	All glass.
				2	1,206	C_3S_2+glass.
65	56.6	25.7	17.7	2	1,215	Glass only.
				1½	1,211	C_3S_2+glass.
66	63.8	22.0	14.2	2	1,206	Glass only.
				1½	1,190	C_3S_2+glass.

[a] By analysis.
[b] R_2O_3.

4. $2CaO.SiO_2$

The data on preparations determining the area within which dicalcium silicate occurs as the primary phase are given in table 4. The phenomenon of resorption, which has been fully discussed by Rankin and Wright [3], is found to occur during the crystallization of a number of these preparations. Numbers 71, 73, 74, 76, and 77 illustrate the progressive phase relations with regard to resorption of all compositions within the area $3CaO.2SiO_2$-b-A (fig. 2). The boundary between the fields of dicalcium silicate and dicalcium ferrite could not be located satisfactorily by means of quenching experiments, because the preparations were characterized by profuse quench crystals of the calcium ferrites. The determination of the primary phase in the region of this boundary would require a clearer distinction than has been found between ferrite crystals formed on quenching and those that are in equilibrium with liquid at the temperatures of the quench.

It has been shown that the formation of two limited solid-solution series between the calcium borates and dicalcium silicate has a marked effect upon the α-β inversion temperature and upon the index of refraction of the dicalcium silicate [13]. The addition of Fe_2O_3 to $2CaO{\cdot}SiO_2$ causes a maximum lowering of the α-β inversion temperature of about 60 degrees (table 5 and fig. 3). Since the addition of 0.5 percent of Fe_2O_3 by weight causes a lowering of the inversion temperature of 60 degrees and the addition of larger percentages causes no further lowering, it is believed that the limit of solid solution of Fe_2O_3 in dicalcium silicate is not more than 0.5 percent. No varia-

tion in the indices of the dicalcium silicate was noted—thus this property cannot be used to indicate the presence of solid solution.

The extent of the solid solution of Fe_2O_3 in β-dicalcium silicate was determined also by treating mixtures of these two materials at appropriate temperatures below the melting points of either material, quenching, and examining microscopically for the presence of glass.[2] Dicalcium silicate prepared in the ordinary way proved unsuitable for this purpose, since the compound on quenching always inverted to the low temperature (γ) form. However, if the initial mixture was prepared from the crystalline, hydrated, dicalcium silicate $10CaO \cdot 5SiO_2 \cdot 6H_2O$, this inversion did not occur.

In discussing their experiments on the hydration of dicalcium silicate, Keevil and Thorvaldson [14] describe three crystalline forms

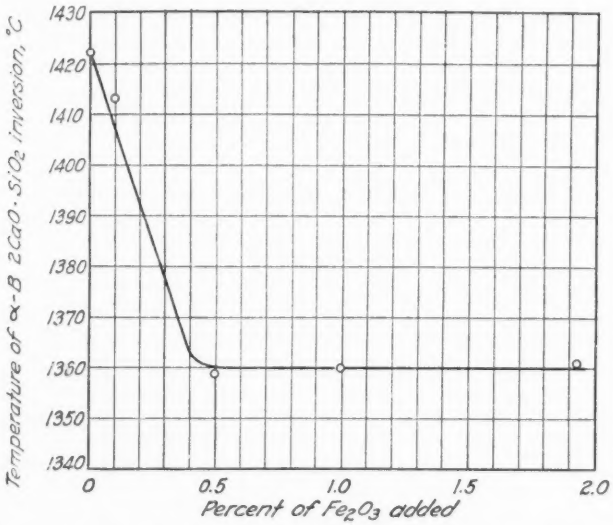


FIGURE 3.—*Effect of* Fe_2O_3 *on the* α-β-$2CaO.SiO_2$ *inversion temperature.*

of hydrated dicalcium silicate. It was reported that two forms retained their original crystal structure after ignition at 900° C and possessed indices of refraction considerably lower than the lower index of β-dicalcium silicate but well above those of γ-dicalcium silicate. The third and most distinctive product found in steam-treated dicalcium silicate was described as well-developed, platelike, orthorhombic crystals, with refractive indices: $\alpha = 1.610 \pm 0.002$ and $\gamma = 1{,}633 \pm 0.002$. The dehydration of this product was not discussed. Flint, McMurdie, and Wells [15] duplicated this product and suggested for it the formula $10CaO \cdot 5SiO_2 \cdot 6H_2O$.

Experiments in the present study proved that the treatment of $10CaO \cdot 5SiO_2 \cdot 6H_2O$ at 1,450° C resulted in β-dicalcium silicate. It is of interest to note that, (1) the platelike form is not retained, but instead the irregularly shaped crystals of β-dicalcium silicate are

[2] If the dicalcium silicate is able to take up some ferric oxide in solid solution, a preparation composed of dicalcium silicate and an amount of Fe_2O_3 smaller than or equal to the limiting amount that could be held in solid solution should not form any liquid when treated at a temperature well below the melting point of dicalcium silicate. For this reason, the presence of glass in a preparation treated as above indicates that the amount of Fe_2O_3 in the mixture exceeds the amount that can be held in solid solution.

observed, (2) normal indices of refraction for β-dicalcium silicate are obtained, and (3) the β-γ inversion is prevented. Keevil and Thorvaldson suggest that the finely divided form of their dehydrated products prevents the inversion of the β-form to the γ-form. However, it is here shown that dehydrated $10CaO \cdot 5SiO_2 \cdot 6H_2O$ does not invert to the γ-form, even though occurring in large crystals.

Mixtures of dicalcium silicate and ferric oxide containing 2 percent, 1 percent, and 0.5 percent of ferric oxide, treated for 17 hours at 1,350° to 1,360° C, consisted, upon quenching, of β-$2CaO \cdot SiO_2$ and glass. Thus, if there is solid solution of ferric oxide in dicalcium silicate, as indicated by the lowering of the α-β inversion temperature, the limit is probably not more than 0.5 percent of ferric oxide.

The X-ray pattern of a sample of $10CaO \cdot 5SiO_2 \cdot 6H_2O$ treated at 1,350° C for 3 hours was identical with that of ordinary β-dicalcium silicate. However, two mixtures of ferric oxide and dicalcium silicate from the hydrate, containing 0.5 percent and 1 percent of ferric oxide, respectively, gave X-ray patterns in which the lines of dicalcium silicate showed a slight shift. This shift further confirms the presence of a limited solid solution of Fe_2O_3 in dicalcium silicate, as indicated by the α-β inversion lowering.

TABLE 4.—*Composition of and data on preparations determining the dicalcium silicate field*

Preparation number	Composition (percent by weight)			Time at constant temperature	Temperature	Phases (C=CaO; S=SiO_2; F=Fe_2O_3
	Fe_2O_3	CaO	SiO_2			
	%	%	%	*hr*	° *C*	
67	0.5	64.7	34.8	[a]hc	1,414	Eutectic (1).[b]
68	.6	64.8	34.6	hc	1,428	Pseudobinary eutectic (C_2S-C_2F).
69	1.0	64.7	34.3	hc	1,425	Do.
70	2.9	63.8	33.3	hc	1,426	Do.
				¼	1,440	C_2S+glass.
				¼	1,429	Do.
71	6.0	52.0	42.0	¼	1,418	$C_2S+C_3S_2$+glass.
				¼	1,411	Do.
				¼	1,408	C_3S_2+CS+glass.
72	9.6	61.2	29.2	hc	1,426	Pseudobinary eutectic (C_2S-C_2F).
				¼	1,422	Glass only.
				¼	1,414	C_2S+glass.
73	10.0	50.0	40.0	¼	1,406	$C_2S+C_3S_2$+glass.
				¼	1,397	Do.
				¼	1,378	Do.
				¼	1,359	C_3S_2+CS+glass.
				¼	1,410	Glass only.
				¼	1,386	C_2S+glass.
74	18.0	46.0	36.0	¼	1,361	$C_2S+C_3S_2$+glass.
				¼	1,338	C_3S_2+glass.
				¼	1,301	Do.
				¼	1,252	C_3S_2+CS+glass.
				¼	1,396	Glass only.
75	24.0	44.0	32.0	¼	1,375	C_2S+glass.
				¼	1,300	$C_2S+C_3S_2$+glass.
				¼	1,331	C_2S+glass.
				¼	1,301	$C_2S+C_3S_2$+glass.
76	28.0	41.6	30.4	¼	1,278	Do.
				¼	1,238	C_3S_2+glass.
				¼	1,291	C_3S+glass.
77	32.0	40.0	28.0	¼	1,240	$C_3S+C_3S_2$+glass.
				¼	1,219	C_3S_2+glass.
78	34.0	40.0	26.0	¼	1,285	C_3S+glass.
79	34.0	52.0	14.0	¼	1,412	Do.

[a] hc indicates data obtained from heating curves. Under the column headed "Phases," the data given in such cases represent interpretations placed on breaks of heating curves.

[b] Numbers in parentheses refer to points in figure 2.

TABLE 4.—*Composition of and data on preparations determining the dicalcium silicate field*—Continued

Preparation number	Composition (percent by weight)			Time at constant temperature	Temperature	Phases (C=CaO; S=SiO_2; F=Fe_2O_3)
	Fe_2O_3	CaO	SiO_2			
	%	%	%	*hr*	° *C*	
80	35.0	42.4	22.6	¼	1,504	Glass only.
				¼	1,494	C_2S+glass.
81	36.0	38.0	26.0	¼	1,279	Do.
				¼	1,248	C_2S+C_3S_2+glass.
				¼	1,236	Do.
				¼	1,232	Do.
82	36.0	40.0	24.0	¼	1,369	C_2S+glass.
				¼	1,349	Do.
				¼	1,198	C_2S+C_3S_2+glass.
83	36.8	39.2	24.0	¼	1,324	C_2S+glass.
				¼	1,227	Do.
84	38.0	38.0	24.0	¼	1,247	Do.
				¼	1,241	C_2S+C_3S_2+glass.
85	38.0	40.0	22.0	¼	1,458	C_2S+glass.
86	38.8	52.0	9.2	¼	1,494	Do.
87	39.2	36.8	24.0	¼	1,297	Do.
				¼	1,250	C_2S+C_3S_2+glass.
88	40.0	39.0	21.0	hc	1,402	Liquidus.
				½	1,407	Glass only.
				½	1,400	C_2S+glass.
89	40.0	42.0	18.0	¼	1,528	Do.
				hc	1,215	Boundary.
90	42.0	36.0	22.0	¼	1,257	C_2S+glass.
				hc	1,237	Boundary.
91	42.0	40.0	18.0	¼	1,207	C_2S+C_3S_2+glass.
				¼	1,466	C_2S+glass.
92	42.0	50.0	8.0	¼	1,472	Do.
93	44.0	34.0	22.0	1	1,244	Glass only.
				1	1,220	C_2S+C_3S_2+glass.
94	44.0	38.0	18.0	¼	1,464	Glass only.
				¼	1,450	C_2S+glass.
95	46.0	36.0	18.0	¾	1,364	Do.
96	46.0	40.0	14.0	¼	1,500	Glass only.
				¼	1,462	C_2S+glass.
97	46.0	48.0	6.0	¼	1,441	Do.
98	48.0	34.0	18.0	¼	1,336	Glass only.
				¼	1,319	C_2S+glass.
99	48.0	44.0	8.0	¼	1,446	Do.
100	48.0	46.0	6.0	¼	1,445	Do.
101	50.0	32.0	18.0	¾	1,233	Glass only.
				¾	1,220	C_2S+glass.
102	50.4	38.4	11.2	½	1,545	Glass only.
				½	1,510	C_2S+glass.
103	50.8	32.0	17.2	½	1,270	Glass only.
				½	1,260	C_2S+glass.
104	52.0	38.0	10.0	¼	1,512	Do.
105	52.0	42.0	6.0	¼	1,467	Glass only.
				¼	1,440	C_2S+glass.
106	54.0	30.0	16.0	1½	1,240	Glass only.
				2	1,218	C_2S+glass.
107	54.0	32.0	14.0	¼	1,251	Do.
108	54.0	40.0	6.0	¼	1,460	Glass only.
				¼	1,429	C_2S+glass.
109	56.0	38.0	6.0	¼	1,431	Glass only.
				¼	1,425	C_2S+glass.
110	58.0	30.0	12.0	½	1,300	Glass only.
				½	1,280	C_2S+glass.
111	58.8	26.8	14.4	½	1,245	Glass only.
				¾	1,224	C_2S+glass.
				2	1,206	C_2S+C_3S_2+glass.
112	58.8	34.0	7.2	½	1,402	Glass only.
				½	1,390	C_2S+glass.
113	60.0	28.0	12.0	½	1,251	Glass only.
				½	1,225	C_2S+glass.
114	60.8	32.0	7.2	½	1,380	Glass only.
				½	1,362	C_2S+glass.
115	62.0	27.9	10.1	3	1,200	Do.
116	62.8	30.0	7.2	1	1,358	Glass only.
				1	1,348	C_2S+glass.

TABLE 5.—*Data showing the lowering of the α-β dicalcium silicate inversion temperature and determining the temperature of eutectics (1) and (2)*

Preparation number	Composition (percent by weight)			α-β inversion temperature	Eutectic temperature
	Fe_2O_3	CaO	SiO_2		
	%	%	%	°C.	°C.
117	1.9	63.7	34.4	1,361	
118	1.0	64.4	34.6	1,360	
67	0.5	64.7	34.8	1,359	
136	.1	65.0	34.9	1,413	
86	38.8	52.0	9.2		1,416
97	46.0	48.0	6.0		1,414
119	40.0	50.0	10.0		1,412
67	0.5	64.7	34.8		1,414
				Mean	1,414 Eutectic (1)[a]
120	40.0	54.0	6.0		1,412
121	36.0	56.0	8.0		1,412
122	42.0	52.0	6.0		1,413
123	38.0	54.0	8.0		1,408
				Mean	1,411 Eutectic (2)[a]

[a] Numbers in parentheses refer to points in figure 2.

5. $3CaO \cdot SiO_2$

In table 6 are given the data on preparations that determine the area within which $3CaO \cdot SiO_2$ is the primary phase. The liquidus temperatures rise rapidly along the boundaries from points (1) to (3) and from points (2) to (3). The temperatures available with the furnace used in this study render impossible the location of the upper boundaries of this area.

Point (1) (1,414° C) is the eutectic for α-$2CaO \cdot SiO_2$, $3CaO \cdot SiO_2$, and $2CaO \cdot Fe_2O_3$, while point (2) (1,411° C) is the eutectic for $3CaO \cdot SiO_2$, CaO, and $2CaO \cdot Fe_2O_3$. These temperatures were determined by heating curves and each individual value given in table 5 is the mean of two or more determinations.

The boundary between eutectics (1) and (2) rises to a maximum of 1,428° ±5° C. This temperature is the boundary break on the heating curve of a preparation (50% Fe_2O_3, 46% CaO, 4% SiO_2) on the join $3CaO \cdot SiO_2$-$2CaO \cdot Fe_2O_3$ and in the stability field of $2CaO \cdot Fe_2O_3$.

TABLE 6.—*Composition of and data on preparations determining the tricalcium silicate field*

Preparation number	Composition (percent by weight)			Time at constant temperature	Temperature	Phases (C=CaO; S=SiO_2)
	Fe_2O_3	CaO	SiO_2			
	%	%	%	hr	°C	
124	36.0	54.0	10.0	½	1,530	C_3S+C_2S+glass.
125	37.6	53.2	9.2	½	1,536	C_3S+glass.
126	38.0	54.0	8.0	¼	1,497	Do.
127	40.0	52.0	8.0	¼	1,499	Glass only.
				¼	1,480	C_3S+glass.
122	42.0	52.0	6.0	¼	1,478	Do.
128	44.0	50.0	6.0	¼	1,468	Glass only.
				¼	1,449	C_2S+glass.
129	45.6	49.2	5.2	¼	1,429	Glass only.
				¼	1,412	C_2S+CaO+glass.

6. CaO

The data on several preparations in which CaO occurs as the primary phase are given in table 7.

TABLE 7.—*Composition of and data on preparations determining the calcium oxide field*

Preparation number	Composition (percentage by weight)			Time at constant temperature	Temperature	Phases (C=CaO; S=SiO_2; F=Fe_2O_3)
	Fe_2O_3	CaO	SiO_2			
	%	%	%	*hr*	°C	
121	36.0	56.0	8.0	¼	1,532	CaO+C_2S+glass.
120	40.0	54.0	6.0	¼	1,480	CaO+glass.
130	44.0	52.0	4.0	¼	1,446	Do.
131	46.0	50.0	4.0	¼	1,447	Do.
				¼	1,427	CaO+C_2S+glass.
132	48.0	48.0	4.0	¼	1,443	Glass only.
				¼	1,435	CaO+glass.
				¼	1,348	CaO+C_2S+C_4F.

IV. REDUCTION OF FERRIC OXIDE IN TERNARY MIXTURES

The reduction of ferric oxide in the system CaO-Fe_2O_3 [6] was reported as negligible in mixtures containing less than about 74 percent by weight of ferric oxide. Since some of the ternary mixtures developed magnetic properties after treatment at high temperatures, an indication of the amount of reduction of Fe_2O_3 was desired. Determinations of ferrous oxide were made on several charges containing between 12 and 63 percent of ferric oxide and between 6 and 56 percent of silica and located in the various fields delimited. The preparations used in these tests were wrapped in platinum foil, treated at about their liquidus temperature for 15 minutes, and quenched in air. The resulting material was coarsely ground and the platinum separated by means of a sieve. Weighed samples were treated with hot dilute HCl in an atmosphere of carbon dioxide until all except the silica was dissolved. The solution was diluted with air-free water, a phosphoric and sulfuric acid mixture was added, and the ferrous oxide determined by titration with potassium dichromate.

TABLE 8.—*Ferrous oxide content of several representative preparations*

Preparation number	Composition (percentage by weight)			Primary phase (C=CaO; S=SiO_2)	Temperature	Time at constant temperature	FeO
	Fe_2O_3	CaO	SiO_2				
	%	%	%		°C	*hr*	%
66	63.8	22.0	14.2	C_3S_2	1,200	¼	0.7
109	56.0	38.0	6.0	C_2S	1,400	¼	1.0
133	48.0	38.0	14.0	C_2S	1,400	¼	1.1
128	44.0	50.0	6.0	C_2S	1,400	¼	0.0
15	40.1	19.2	40.7	SiO_2	1,300	¼	2.8
41	40.0	32.0	28.0	CS	1,250	¼	0.9
134[1]	35.8	37.5	26.8	C_2S	1,410	¼	.8
135[1]	31.6	33.1	35.2	CS	1,400	¼	3.0
35	16.0	46.0	38.0	CS	1,400	¼	0.9
23	12.0	32.0	56.0	CS	1,350	¼	3.1

[1] These compositions were prepared and analyzed in connection with another study and were treated at about 100° C above their liquidus temperatures.

The results are given in table 8. The reduction of ferric oxide increases with the temperature and with the amount of silica present.

the latter appearing to be the more potent factor. The amounts of ferrous oxide found are not believed to cause a significant error in the diagram.

V. APPLICATIONS

The specifications generally in use for either moderate or low heat of hydration cements, and for sulfate-resisting cements, demand a low alumina and a high iron oxide content. Consequently, the data obtained in this investigation are of interest industrially in the production of such cements. The following indicate certain applications.

It has been shown by Kühl [16] that cements of the portland cement type can be produced in the system lime-ferric oxide-silica. The composition range of alumina-free cements having satisfactory strengths and setting properties has been delimited by Kühl as being within the elliptical area enclosed by a continuous line in figure 2. For comparison, the field representing the compositions of portland cement in the system lime-silica-R_2O_3, in which R_2O_3 is considered as alumina, has been indicated by the elliptical area within the broken line. As can be seen, the substitution of ferric oxide for alumina results in a marked enlargement of the field in which satisfactory cements can be obtained.

Bogue [17] has described the manner in which the oxide components of portland cement containing SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO, alone, react or combine:

(1) The ferric oxide reacts with alumina and lime to form $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$.

(2) The magnesia remains essentially in the form of uncombined MgO.

(3) The alumina remaining after the formation of the compound $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ reacts with lime to form $3CaO \cdot Al_2O_3$.

(4) The lime remaining after the formation of the above compounds reacts with silica. The compound $2CaO \cdot SiO_2$ is formed, and any CaO then uncombined reacts with the $2CaO \cdot SiO_2$ to form $3CaO \cdot SiO_2$. If CaO remains after converting all of the $2CaO \cdot SiO_2$ to $3CaO \cdot SiO_2$, it will be present as uncombined lime.

When the R_2O_3 content of cements containing SiO_2, Al_2O_3, Fe_2O_3, and CaO, alone, is predominately ferric oxide, the limit of lime content is decreased because of the difference in combining ratios of the aluminum and ferric oxides. In such portland cements the alumina reacting with lime to form $3CaO \cdot Al_2O_3$ requires 1.65 parts of CaO for 1 part of alumina, but in the iron-rich cements the ferric oxide not in solid solution with dicalcium silicate or in combination as $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ probably forms dicalcium ferrite, in which 1 part of ferric oxide requires only 0.70 part of CaO. Thus more lime remains for combination with silica and the minimum lime content is lowered.

Lowering the SiO_2-R_2O_3 ratio in portland cements having an Al_2O_3-Fe_2O_3 ratio of between 0.6 and 1.6 results in the formation of increasing amounts of tricalcium aluminate. If this compound is in excess, difficulty with rapid setting of the cement is encountered. Lower SiO_2-R_2O_3 ratios are possible in iron-rich cements than in the portland type because of the formation of dicalcium ferrite, which hydrates rapidly but does not have the flash-setting property characteristic of tricalcium aluminate.

The liquidus temperatures of preparations within the dicalcium silicate field of the system lime-alumina-silica are lowered little, if any, by the substitution of ferric oxide for alumina, but the temperature at which liquid is first formed is appreciably reduced. The majority of modern portland cement compositions are within the triangle $2CaO{\cdot}SiO_2$-$3CaO{\cdot}SiO_2$-$3CaO{\cdot}Al_2O_3$ of the system lime-alumina-silica. Compositions within this area have a eutectic temperature of 1,455° C. Substitution of ferric oxide for alumina, a condition which is approached in the case of high-iron cements, results in eutectic temperatures of 1,411° C for the triangle $3CaO{\cdot}SiO_2$-CaO-$2CaO{\cdot}Fe_2O_3$ or 1,414° C for the triangle $2CaO{\cdot}SiO_2$-$3CaO{\cdot}SiO_2$-$2CaO{\cdot}Fe_2O_3$.

An interesting relationship is observed by comparing the amounts of liquid formed at a given temperature in various cement mixtures. In table 9 are listed five oxide compositions which lie in the cement zone of the system lime-ferric oxide-silica, together with the percentage of liquid at 1,455° C, when the R_2O_3 is all Al_2O_3 and when it consists of Fe_2O_3. It is seen that, although the use of ferric oxide brings about the formation of liquid at lower temperatures than alumina does, the ferric oxide mixtures result in the formation of smaller amounts of liquid than those in which alumina is used.

TABLE 9.—*Liquid content of cement mixtures in the system lime-ferric oxide-silica at 1,455° C*

[The amount of liquid that would result from a percentage substitution of Al_2O_3 for Fe_2O_3 in these mixtures is also given]

Number	Composition (percentage by weight)			Percentage liquid when—	
	CaO	SiO_2	R_2O_3	$R_2O_3 = Fe_2O_3$	$R_2O_3 = Al_2O_3$
	%	%	%	%	%
1	64	30	6	13	18
2	62	28	10	22	31
3	62	24	14	31	43
4	66	20	14	31	42
5	68	26	6	13	19

VI. SUMMARY

The boundaries of the primary phase areas in a part of the ternary system lime-ferric oxide-silica have been established.

The effect of ferric oxide in lowering the α-β inversion temperature is offered as evidence of a limited solid solution of ferric oxide in dicalcium silicate. The limit of this solid solution is placed at not more than 0.5 percent by weight of ferric oxide. No variation in the indices of refraction of the dicalcium silicate due to solid solution was noted. However, the presence of as little as 0.5 percent of ferric oxide caused a slight shift of the lines in the X-ray patterns. The crystalline hydrated dicalcium silicate $10CaO{\cdot}5SiO_2{\cdot}6H_2O$, after treatment at 1,350° C, could be quenched to maintain the β-form of dicalcium silicate as verified by its X-ray pattern. Ferric oxide did not prevent the β-γ inversion in quenched samples prepared from calcium carbonate and silica gel.

No ternary compounds were found in the portion of the system investigated.

The amount of ferrous oxide developed as a result of heating preparations in several stability fields at their liquidus temperatures for 15 minutes was determined and found to increase with increase of temperature and with higher silica contents. The largest percentage of ferrous oxide found was about 3, which was not believed to cause a significant error in the results.

The author is indebted to H. F. McMurdie for the X-ray patterns, and acknowledges the cooperation and advice of L. S. Wells and of E. P. Flint.

VII. REFERENCES

[1] Hansen and Bogue, *Studies on the system calcium oxide-ferric oxide-silica*, J. Am. Chem. Soc. **48,** 1261 (1926).
[2] A. L. Day, E. S. Shepherd, and F. E. Wright, *The lime-silica series of minerals*, Am. J. Sci. [4] **22,** 265–302 (1906).
[3] G. A. Rankin and F. E. Wright, *The ternary system* CaO-Al_2O_3-SiO_2. Am. J. Sci. [4] **39,** 1–79 (1915).
[4] J. B. Ferguson and H. E. Merwin, *The ternary system* CaO-MgO-SiO_2. Am. J. Sci. [4] **48,** 81–123 (1919).
[5] J. W. Grieg, *Immiscibility of silicate melts.* Am. J. Sci. [5] **13,** 1–44, 133–154 (1927).
[6] R. B. Sosman and H. E. Merwin, *The system* CaO-Fe_2O_3. J. Wash. Acad. Sci. **6,** 532–537 (1916).
[7] N. L. Bowen, J. F. Schairer and H. W. V. Willems, *The system* Na_2SiO_3-Fe_2O_3-SiO_2. Am. J. Sci. [5] **20,** 405–455 (1930).
[8] H. S. Roberts, *The Geophysical Laboratory furnace thermostat*, J. Opt. Soc. Am. Rev. Sci. Instr. **11,** 171–186 (1925).
[9] C. N. Fenner, *The stability relations of the silica minerals*, Am. J. Sci. [4] **36,** 351 (1913).
[10] N. L. Bowen, J. F. Schairer, and E. Posnjak, *The system* CaO-FeO-SiO_2. Am. J. Sci. [5] **27,** 206 (1933).
[11] Kiezo Iwase and Usaburo Nishioka, *The equilibrium diagrams of three binary systems*, (1) $CaO.SiO_2.TiO_2$-$MgO.TiO_2$, (2) $CaO.MgO.2SiO_2$-$MnO.TiO_2$ and (3) $CaO.SiO_2$-$2CaO.Fe_2O_3$. Sci. Rep., Tohoku Imp. Univ. [1] **26,** 592–601 (1938).
[12] G. Sitz, *The system* $CaO.Fe_2O_3.SiO_2$ *in relation to its significance for metallurgical slags*, Metall u. Erz **29,** 269 (1932).
[13] E. P. Flint and L. S. Wells, *The system lime-boric oxide-silica.* J. Research NBS **17,** 727–752 (1936) RP941.
[14] N. B. Keevil and T. Thorvaldson, *The hydration of dicalciums ilicate and tricalcium silicate*, Canadian J. Research **14,** 20–30 (1936).
[15] E. P. Flint, H. F. McMurdie, and L. S. Wells, *Formation of hydrated calcium silicates at elevated temperatures and pressures*, J. Research NBS **21,** 617–638 (1938) RP1147.
[16] Hans Kühl, *The cement field in the ternary system lime-ferric oxide-silica*, Zement **13,** 25 et seq. (1924).
[17] R. H. Bogue, *Calculation of the compounds of portland cement.* Ind. Eng. Chem. Anal. Ed. **1,** 192 (1929).
[18] Int. Crit. Tables **1,** 154 (McGraw-Hill Book Co., Inc., New York, N. Y., 1926).

WASHINGTON, August 30, 1940.